Title: Pressure Induced Metallization of the Perovskite Sr(3)Fe(2)O(7)

Author(s): G.Kh. Rozenberg
          G.Yu. Machavariani
          M.P. Pasternak
          A.P. Milner
          G.R. Hearne
          R.D. Taylor
          P. Adler

Submitted to: Physica Status Solid and meeting of High Pressure Semiconductors

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
PRESSURE INDUCED METALLIZATION OF THE PEROVSKITE \( \text{Sr}_3\text{Fe}_2\text{O}_7 \)

G.Kh. Rozenberg\(^a\), G.Yu. Machavariani\(^a\), M.P. Pasternak\(^a\), A. P. Milner\(^a\),

G.R. Hearne\(^b\), R.D. Taylor\(^c\), and P. Adler\(^d\)

\(^a\)School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel

\(^b\)Department of Physics, University of the Witwatersrand, P O Wits 2050, Johannesburg-Gauteng, South Africa

\(^c\)MST10, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

\(^d\)Max Planck Institut für Festkörperforschung, 70569 Stuttgart, Germany
Electrical, magnetic and structural properties of the antiferromagnetic semiconductor Sr$_2$Fe$_2$O$_7$ (Fe$^{4+}$, $d^4$) were probed by resistance, Mössbauer spectroscopy (MS) and X-ray diffraction (XRD) measurements to $P \sim 40$ GPa using diamond-anvil cells. A sluggish pressure-induced insulator-metal transition is observed with a clear incipient metallic state at $P \geq 20$ GPa. The Fe(IV) 3$d$ magnetic moments remain unaltered across the transition as deduced from MS, and XRD studies show no structural symmetry change to 40 GPa. The results are consistent with carrier delocalization due to $p$-$p$ gap closure e.g., ligand-to-ligand charge transfer that does not involve the $d$-states and structural symmetry changes.

PACS numbers: 71.28.+d, 71.30.+h, 62.50.+p, 76.80.+y

Substance classification: S1.1
INTRODUCTION

It is now well documented that the transition-metal (TM) compounds can be classified into two regimes according to relative magnitudes of the ligand-to-metal charge transfer energy $\Delta$, and the intra-atomic $d$-$d$ Coulomb energy $U$. In the Mott-Hubbard regime, where $\Delta > U$, the band gap corresponds to charge fluctuations of $d$-$d$ type, $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$. Alternatively, if $U > \Delta$, compounds will have an insulating charge-transfer (C-T) energy gap, where ligand-to-metal charge fluctuations $d^n + d^n \rightarrow d^{n+1} + d^n L$ ($L$ is a hole in the ligand band) are expected to occur [1,2]. $\Delta$ decreases with increasing atomic number of the TM cations as well as with increasing oxidation state for a given TM ion [2]. This trend may lead in some cases to a vanishing or even negative values of $\Delta$. For small $p$-$d$ hybridization those systems will be metallic as a result of the $p$-band and the upper Hubbard sub-band overlap. However, for a sizable enough hybridization the two overlapping bands may split leading to a gapped state and a covalent insulator [3,4]. The ground state of the covalent insulator is dominated by a $d^{n+1} L$ configuration rather than $d^n$ and carrier delocalization leading to a metallic state will be brought about via ligand-to-ligand charge transfer.

As mentioned, the IM transition of this type may occur in high-valence Fe compounds such as the strontium ferrates where Fe is in the formal 4+ oxidation state. SrFeO$_3$ (n=0) 3-D antiferromagnetic perovskite has a high electronic conductivity and may be an example of a correlated metal. It exhibits a transition to semiconductor state if the oxygen stoichiometry is changed [5]. However the 2-D antiferromagnetic semiconductor Sr$_2$FeO$_4$ (n=1) with the K$_2$NiF$_4$-type structure is quite different. Recent studies of Sr$_2$FeO$_4$ by Rozenberg et al. [6] gave the first compelling experimental evidence for the presence and pressure-induced closure of a $p$-$p$ gap resulting in a metallic state. Sr$_3$Fe$_2$O$_7$ (n=2), a Ruddlesden-Popper derivative of the K$_2$NiF$_4$ structure [7] consists of nearly isolated double-sheets in of FeO$_6$ octahedra in contrast to single sheets in Sr$_2$FeO$_4$.

In the series of Sr$_{n+1}$Fe$_n$O$_{3n+1}$ compounds the bond lengths and structure of Fe-O within the [FeO$_6$]$^8^-$ clusters are quite similar. Therefore it is expected that the electronic behavior of the strontium ferrates is determined by the distinct bandwidths arising from the different inter-cluster coupling, within the respective crystals structures. Thus the present studies of
Sr$_3$Fe$_2$O$_7$, by concurrent monitoring the electrical-transport, magnetic, and crystallographic properties are expected to elucidate the role of the inter-cluster in determining the nature of the ligand $p$-$p$ gap.

**EXPERIMENTAL**

Sr$_3$Fe$_2$O$_7$ was synthesized from stoichiometric amounts of SrO and $\alpha$-Fe$_2$O$_3$ enriched with $^{57}$Fe using the method described by Adler [8]. To assure the high oxygen content needed for the reaction, the reaction took place at oxygen pressure of 60 MPa and 500 °C for 18 hours using an autoclave. The sample quality was determined by XRD.

Miniature DACs [9] of the opposing plates (Merrill-Bassett) type were used for resistance, MS, and XRD measurements. Samples mixed with small ruby chips, used as pressure markers [10], were loaded into cavities typically of 200 - 250 μm diameter and 30-40 μm thickness, drilled in Ta$_{90}$W$_{10}$ or 310S stainless steel gaskets. Argon was used as a pressure-transmitting medium both for XRD and MS pressure studies. No pressure transmitting medium was used for resistance measurements.

*Resistance measurements.* The sample/metal-gasket cavity were coated with an insulating mixture of Al$_2$O$_3$/NaCl combined with epoxy. Four-probe DC resistance measurements were carried out with 5-7 μm-thick foil Pt electrodes as a function of temperature and pressure [11]. The pressure distribution for the resistance studies was typically 5-10 % of the average pressure.

Pressure and temperature $^{57}$Fe Mössbauer experiments were performed using a top-loading cryostat using a 10 mCi $^{57}$Co(Rh) point source of 0.5mm × 0.5mm areal dimensions in conjunction with a Kr-CO$_2$ proportional counter; for further details see Ref. 12. All spectra were analyzed using appropriate least-squares-fitting programs to obtain the hyperfine interaction parameters.

High pressure X-ray diffraction studies were performed in the B1 station of the Cornell High Energy Synchrotron Source (CHESS) in the energy-dispersive mode. Data were recorded at ~295 K with a scattering angle of 2\theta = 7.909°.

**RESULTS.**
The X-ray powder diagrams of Sr$_3$Fe$_2$O$_7$ reveal Bragg reflections consistent with its original tetragonal space group, $I4/mmm$ to the highest pressure measured. The unit cell volume decreased by $\sim 16\%$ upon compression from ambient pressure to 35 GPa (see Fig. 1). From early neutron diffraction studies [7] of Sr$_3$Fe$_2$O$_7.5$ it was shown that the lattice parameter $a$ decreases linearly with decreasing $\delta$, i.e. with increasing Fe$^{4+}$ content. From the measured $a$ parameter in our sample one derives the composition Sr$_3$Fe$_2$O$_{6.94}$. The equation of state was analyzed using a Birch-Murnaghan (Eulerian) third-order finite-strain equation of state formalism [13] and is depicted in Fig. 1 as a solid curve through the experimental points.

The temperature-dependent resistance studies, $R(P,T)$, provide the definite experimental evidence for the onset of the IM transition with pressure increase (see Fig. 2). The onset of a metallic state at $P \geq 20$ GPa was deduced from the change in sign of $dR/dT$, from negative to positive. All the $R(P,T)$ curves beyond 20 GPa show a minimum which moves to lower temperatures as pressure is increased.

We could not fit the conductance vs. temperature dependence with a single universal law which could encompass the whole temperature range. Conductance ($\sigma$) variations with temperature ($T$) were first plotted in the form of log $\sigma$ vs. $T^{-1}$ for different temperature ranges but without success. However in the $10 < T < 120$ K temperature range $\sigma(T)$ of the form,

$$\sigma = A \exp[-(T/T_0)^{1/4}],$$

conformed well with our experimental results (see Fig. 3). As suggested by Mott [14] expression (1) can be associated with the \textit{variable-range hopping} of carriers between localized states.

\textit{Mössbauer spectra} at ambient and low pressures at $T < T_N$ are characterized by two distinct magnetic sites with hyperfine fields $B_{hf}$ of 28 and 42 T, and isomer shift (IS) values of -0.06 and 0.32 mm/s, respectively (see Fig. 4). These two distinct sites persist to pressures of $\sim 12$ GPa with $B_{hf}$ very similar to the values at ambient pressure. Spectra recorded in the range 21 - 40 GPa could be fitted with a single magnetic component indicative of all iron sites having identical magnetic-electronic structure. It should be noted that for $P \geq 24$ GPa, $T_N \geq 300$ K. A
detailed discussion concerning the interesting magnetic properties of the 2-D antiferromagnetic Sr$_3$Fe$_2$O$_7$ will be published elsewhere.

4. DISCUSSION AND CONCLUSIONS

The combined experiments of $R(P,T)$ and XRD(P) show that the pressure-driven IM transition is not accompanied by a crystallographic phase transition. The pressure-induced gap closures of the M-H intra-band, the C-T inter-band, and the $p$-$p$ intra-band systems can all be attained via an isostructural IM transition. However the persistence of the magnetic state to pressures beyond the transition compel us to discount the M-H or C-T gap closure as the mechanism responsible for metallization. In the latter cases because of the collapse of correlation inherent to the gap-closure, the 3$d$ magnetic moments must also vanish. Instead, MS data clearly show the presence of magnetic ordering within the metallic state. Thus, the persistence of the magnetic moments can be considered as direct experimental evidence for the existence and subsequent closure of the $p$-$p$ gap in this covalent insulator. Furthermore, the fact that $B_{sf}$ is unaltered at the IM transition shows that the ligand-to-ligand charge transfer due to $d^{n+1}L + d^{n+1}L \rightarrow d^{n+1}L^2$ fluctuations at gap closure barely influences the 3$d$ electronic states.

One of the main features shown by current transport measurements is that the IM transition in Sr$_3$Fe$_2$O$_7$ takes place gradually with pressure increase; thus the Mott temperature $T_o$ (see Eq. 1) decreases continuously with increasing $P$ as shown in the inset of Fig. 3, and no discontinuity is found in the $R(P)$ curve (see inset of Fig. 2). This behavior strongly differs from that of Sr$_2$FeO$_4$ which $R(P,T)$ studies show sharp changes in the electronic state at the iso-structural IM transition [6]. An explanation for this sluggish transition is the possible presence of disorder due to random defects caused by the non-stoichiometry in Sr$_3$Fe$_2$O$_{6.97}$ [15]. Disorder produces Anderson localization at the band edges, and for poor band overlap the states at the Fermi level remain localized, and metallic conduction is hampered. In this regime conduction takes place by *variable-range hopping* of carriers between the defect sites, and the conductivity varies with temperature according to the $T^{-1/4}$ law (see Fig. 3). However at sufficiently high pressure ($P \geq 20$ GPa) the bands will broaden sufficiently, resulting in
extended the states (at the Fermi level) throughout the solid, and the pure metallic state is finally achieved.

Finally it is noteworthy to mention that the Sr$_3$Fe$_2$O$_7$ electronic behavior looks resembles that of SrFeO$_{3.8}$ which shows semi-conducting properties at $\delta > 0$. This system can be chemically altered reaching a metallic state when $\delta \to 0$ [5]. Here $\delta$ plays the same role as $P$ in the case of Sr$_3$Fe$_2$O$_7$. We then conclude that despite the electronic and chemical bond similarities of the intra-cluster $[\text{FeO}_6]^8$ species, the inter-cluster properties within the Sr$_{n+1}$Fe$_n$O$_{3n+1}$ family of compounds ($n = 1,3$) dominate the pressure-induced IM and therefore the nature of the relevant band structure.

ACKNOWLEDGMENTS

We acknowledge the partial support of the USA-Israel Binational Science Foundation BSF #95-00012 and the German-Israel Science foundation GIF #I-086.403 grants. We thank Dr. K.E. Brister for his valuable assistance and guidance at CHESS.
REFERENCES


FIGURE CAPTIONS

Fig. 1. The room-temperature isotherm of Sr$_3$Fe$_2$O$_7$. The solid line is a fit to the experimental points using the Birch-Murnaghan third-order finite-strain equation of state. Parameters derived from this fit are tabulated in the figure.

Fig. 2. Resistance as a function of temperature at selected pressures. Incipient metallic behavior is evident at $P \geq 20$ GPa. The inset shows resistance as a function of pressure at 300 K.

Fig. 3. Temperature dependence of the electrical conductance $\sigma$ of Sr$_3$Fe$_2$O$_7$ under pressure in the temperature range 5 - 300 K. Note the linear relationship of $\ln(\sigma)$ versus $T^{-1/4}$ in the 10 - 100 K range. The inset shows Mott temperature $T_0$ as a function of pressure in this temperature range.

Fig. 4. Mössbauer spectra at of Sr$_3$Fe$_2$O$_7$ at 50 K. The solid lines are theoretical fitting to the data and the dotted curves correspond to the two sites. Up to $\sim 12$ GPa one finds two different sites (see text). At $P \geq 21$ GPa spectra could be fitted with only one site.
Fig. 1

\begin{align*}
K_0 &= 145(3) \text{ GPa} \\
K_i &= 4 \\
V_0 &= 299.7(6) \text{ Å}^3
\end{align*}
Fig. 2
Fig. 3
Fig. 4