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Pressure Induced Metallization of the Perovskite
 $\text{Sr}(\text{Fe}_{2/3}\text{O}_{7/3})$

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PRESSURE INDUCED METALLIZATION OF THE PEROVSKITE $\text{Sr}_3\text{Fe}_2\text{O}_7$

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ABSTRACT

Electrical, magnetic and structural properties of the antiferromagnetic semiconductor $\text{Sr}_3\text{Fe}_2\text{O}_7$ (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) $3d$ 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.

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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 Δ , 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 $d^n + d^n \rightarrow d^{n+1} + d^n \underline{L}$ ($\underline{L}$ is a hole in the ligand band) are expected to occur [1,2]. Δ 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 Δ . 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 $d^{n+1} \underline{L}$ 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_2FeO_4 ($n=1$) with the K_2NiF_4 -type structure is quite different. Recent studies of Sr_2FeO_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. $\text{Sr}_3\text{Fe}_2\text{O}_7$ ($n=2$), a Ruddlesden-Popper derivative of the K_2NiF_4 structure [7] consists of nearly isolated double-sheets in of FeO_6 octahedra in contrast to single sheets in Sr_2FeO_4 .

In the series of $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$ compounds the bond lengths and structure of Fe-O within the $[\text{FeO}_6]^{8-}$ 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

$\text{Sr}_3\text{Fe}_2\text{O}_7$, 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

$\text{Sr}_3\text{Fe}_2\text{O}_7$ was synthesized from stoichiometric amounts of SrO and $\alpha\text{-Fe}_2\text{O}_3$ 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 $\text{Ta}_{90}\text{W}_{10}$ 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 $\text{Al}_2\text{O}_3/\text{NaCl}$ 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 $^{57}\text{Co}(\text{Rh})$ point source of 0.5mm $\times$ 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 $2\theta = 7.909^\circ$.

RESULTS.

The X-ray powder diagrams of $\text{Sr}_3\text{Fe}_2\text{O}_7$ 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 $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ it was shown that the lattice parameter a decreases linearly with decreasing δ , i.e. with increasing Fe^{4+} content. From the measured a parameter in our sample one derives the composition $\text{Sr}_3\text{Fe}_2\text{O}_{6.94}$. 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 (σ) 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,

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

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

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 ~ 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 $\text{Sr}_3\text{Fe}_2\text{O}_7$ will be published elsewhere.

4. DISCUSSION AND CONCLUSIONS

The combined experiments of $R(P,T)$ and $\text{XRD}(P)$ 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 $3d$ 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_{hf} is unaltered at the IM transition shows that the ligand-to-ligand charge transfer due to $d^{n+1} \underline{L} + d^{n+1} \underline{L} \rightarrow d^{n+1} \underline{L}^2$ fluctuations at gap closure barely influences the $3d$ electronic states.

One of the main features shown by current transport measurements is that the IM transition in $\text{Sr}_3\text{Fe}_2\text{O}_7$ 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_2FeO_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 $\text{Sr}_3\text{Fe}_2\text{O}_{6.97}$ [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 $\text{Sr}_3\text{Fe}_2\text{O}_7$ electronic behavior looks resembles that of $\text{SrFeO}_{3-\delta}$ which shows semi-conducting properties at $\delta > 0$. This system can be chemically altered reaching a metallic state when $\delta \rightarrow 0$ [5]. Here δ plays the same role as P in the case of $\text{Sr}_3\text{Fe}_2\text{O}_7$. 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 $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$ family of compounds ($n = 1,3$) dominate the pressure-induced IM and therefore the nature of the relevant band structure.

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FIGURE CAPTIONS

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

Fig. 1

Fig. 2

Fig. 3

Fig. 4