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MÖSSBAUER STUDIES OF Sr_2FeO_4 TO PRESSURES OF 20 GPa

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ABSTRACT

The transport and magnetic properties of the antiferromagnetic semiconductor Sr_2FeO_4 (Fe^{4+}, d^4) were probed by resistance studies and ^{57}Fe Mössbauer spectroscopy to 20 GPa using a diamond-anvil cell. The main conclusions of this work are that beyond the onset of the semiconductor-metal transition at ~17(1) GPa determined in the resistance studies: (1) the compound is still magnetic and, (2) there is no charge disproportionation of the form: $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$. The quadrupole splitting (ΔE_Q) at room temperature (RT) decreases from 0.42 mm/s at ambient pressure to a minimum of 2.2 mm/s at ~5.5 GPa. Beyond 5.5 GPa ΔE_Q at RT increases monotonically reaching 0.5 mm/s at 20 GPa. In the 0-10 GPa pressure range the Néel temperature T_N is pinned at 60-70 K reaching values of 135(5) K at 19 GPa where the compound is metallic. At 19 GPa and $T \ll T_N$ a simplified magnetic spectrum having an internal magnetic field of ~25 T and a substantial quadrupole interaction is obtained.

1. Introduction

The Fe-based perovskites $CaFeO_3$ and $SrFeO_3$ have Fe in the unusually high oxidation state of 4+ ($3d^4$). These compounds had been thoroughly investigated by ^{57}Fe Mössbauer spectroscopy (MS) over an extended temperature and pressure range [1, 2, 3]. Sr_2FeO_4 is another tetravalent Fe-based compound that has been the subject of recent investigations. The compound is an antiferromagnetic semiconductor having $T_N \approx 60$ K. It crystallizes in the tetragonal space group *I 4/mmm*, the K_2NiF_4, structure. This is a 2-D type structure having sheets of FeO_6 octahedra perpendicular to the *c*-axis with each Fe^{4+} ion in D_{4h} (tetragonal) symmetry. Raman and reflectivity pressure studies to 20 and 38 GPa, respectively, have been performed on this compound [4]. In addition to the Raman modes expected for the K_2NiF_4-type structure an additional oxygen-derived mode was evident but disappears at about 5.5 GPa. The optical reflectivity exhibits a dramatic increase in the near-infrared region as pressure is increased beyond 6 GPa and at $P > 13$ GPa it saturates at a considerably higher value compared to ambient pressure. It has been speculated from this behavior that the semiconductor gap narrows under pressure to culminate in a semiconductor-metal transition. In the present study we performed resistance and ^{57}Fe Mössbauer pressure studies using a diamond-anvil cell (DAC) to elucidate the phenomena observed in the Raman and optical reflectivity pressure studies.

2. Experimental

The material was prepared by us from stoichiometric amounts of the oxides by using the method described by Adler [5] . In addition to the main phase consisting of K_2NiF_4 -type Sr_2FeO_4 , a small amount of unreacted Fe_2O_3 was always present even after repeated attempts at synthesis in which conditions were slightly varied. Mössbauer pressure studies were performed on a sample of natural isotopic abundance whose ambient-pressure parameters conformed as close as possible to literature values. Mössbauer studies of the sample at ambient pressure gave the following results : isomer shift (IS) = 0.00(1) mm/s (relative to α-Fe) and $\Delta E_Q \approx 0.42(2)$ mm/s for the simple single-site quadrupole doublet at room temperature, onset of magnetic ordering at $T_N \approx 60$ K, and a complex magnetic spectrum at 33 K, all in accord with previous works [5 ,6].

The sample, mixed with small ruby chips as a pressure marker, was loaded into a cavity drilled in a $Ta_{90}W_{10}$ gasket for MS pressure studies in a Merrill-Basset-type miniature DAC [7], Initial cavity dimensions were 350-μm diameter and 40-μm thickness. The thermal scan method or temperature dependent MS measurements were used to locate the Néel temperature at 9 GPa and 19 GPa, and magnetic spectra were recorded at $T \ll T_N$. Each magnetic spectrum was collected over several days to obtain sufficient statistics for comparison with data at ambient pressure.

3. Results

Temperature dependent resistance R(*T*) measurements in a similar DAC set-up were performed in the same pressure range covered in the Mössbauer studies, namely, to $P \sim 20$ GPa. These studies indicate that a semiconductor-metal transition occurs at 17(1) GPa, see fig. 1.

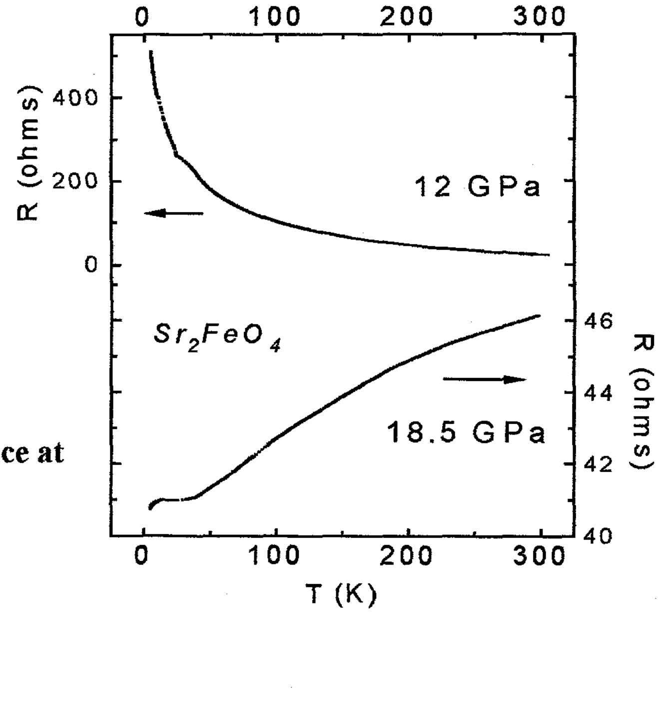

Fig. 1 : Temperature dependence of the resistance at 12 GPa and 18.5 GPa

Mössbauer parameters as a function of pressure derived from the quadrupole doublet at room temperature are plotted in fig. 2. The isomer shift decreases linearly consistent with the increase in density with no indication of discontinuous changes, This finding is consistent with recent X-ray diffraction data that reports no change in crystal structure in this pressure range [8]. However, ΔE_Q reaches a minimum at ~5.5 GPa, (see fig. 2) and increases monotonically for $P > 5.5$ GPa.

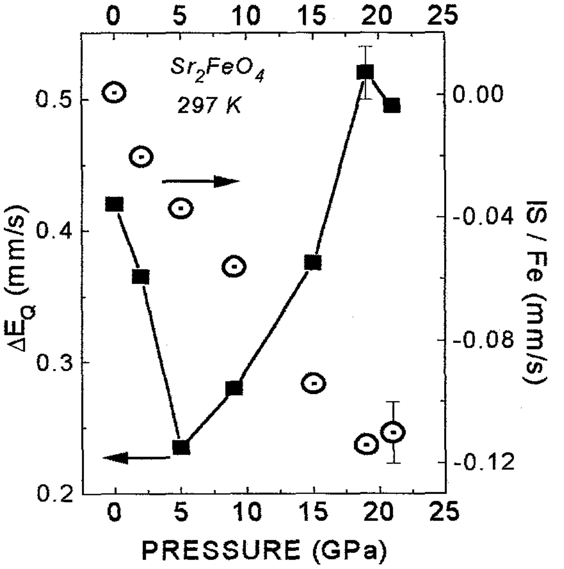

Fig. 2 : Pressure dependence of the isomer shift and quadrupole splitting at room temperature

Low temperature measurements of magnetic spectra are displayed in fig. 3. Thermal scan measurements at 9 GPa show that T_N is in the range 60-70 K. The magnetic spectra display sharper features as compared with the complicated magnetic spectrum at ambient pressure. There at least four Fe sites with internal magnetic fields H_{hf} in the range 26-33 T were derived [6]. At 19 GPa the magnetic spectrum has sharpened even further, considerably simplified compared with spectra at lower pressures. The maximum value of H_{hf} is estimated to be ~25 T and there is a very substantial quadrupole shift. Temperature dependent MS data locates T_N to be in the range 130 -140 K.

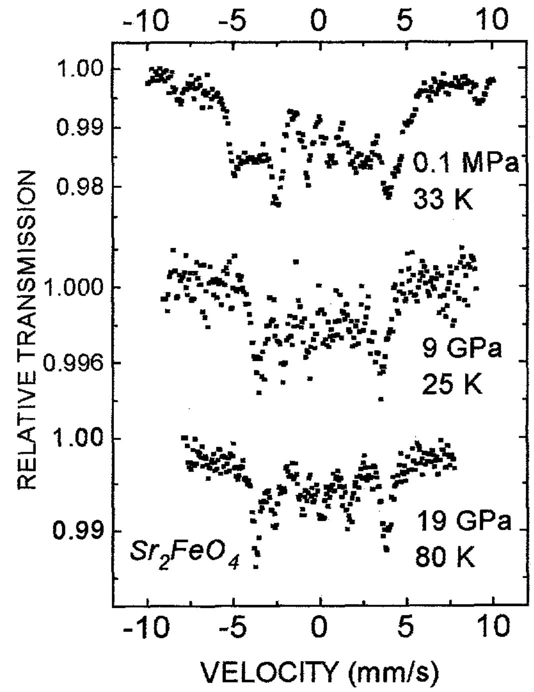

Fig. 3 : Magnetic spectra at cryogenic temperatures as a function of pressure.

4. Discussion

The Fe local environment is a slightly elongated octahedron with Fe-O bond distances of 4 × 1.932 Å and 2 × 1.950 Å under ambient condition [6]. As the *c/a* ratio of the tetragonal unit cell is decreased under pressure the octahedron's Fe-O bonds become more symmetric with bond lengths almost equal to each other . This explain the decrease in the electric-field gradient (EFG) and hence ΔE_Q attaining a minimum value at ~ 5 GPa (see fig. 2). Further increase of pressure, beyond the value corresponding to a symmetric octahedon changes the *c/a* values resulting in the renewing of a distorted octahedron. This increase the crystal-field splitting and consequently leads to an increase in the EFG. At

P~ 5.5 GPa the oxygen-derived Raman mode disappears [4] possibly because it ceases to be Raman-active in a tetragonal unit cell having regular FeO_6 octahedral units.

The main conclusions derived from the MS experiments at low temperatures are: (1) in the metallic state the compound is still magnetic ($T_N \sim 130$ K). (2) The spin arrangement originally deduced to be of a spiral-type in the 2-D K_2NiF_4-type structure at ambient pressure [6], changes considerably under pressure. (3) There is no evidence of charge disproportionation of the type $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$. (4) Electronic and magnetic properties in the metallic state of Sr_2FeO_4 are similar to that of the cubic perovskite $SrFeO_3$ which is metallic and magnetic ($T_N \approx 131$ K) albeit at ambient pressure [2].

For compounds having the transition-metal in a high formal oxidation state, carrier delocalization leading to a metallic state is supposed to occur by **ligand-to-ligand** charge transfer [9]. This mode of *charge transfer* is not a Mott transition barely influencing the magnetic moment at the Fe atom in Sr_2FeO_4, Such a pressure induced *insulator-metal* transition will preserve the magnetic moment and magnetism below T_N.

Acknowledgment

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