

# Metallic Transition of the Colossal Magnetoresistance Material $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ( $x = 0.18$ ) under High Pressure

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A pressure-induced phase transition in the colossal magnetoresistance (CMR) material  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$  was studied by using infrared (IR) reflection and X-ray diffraction (XRD) at pressures up to 40 GPa at room temperature. XRD shows that the crystal structure of this sample is a NaCl-type structure at ambient pressure, that a structural change starts around 17 GPa, and that a mixed phase mixed between the NaCl-type low-pressure phase and an unknown structure high pressure phase continues up to around 25 GPa. On the other hand, the IR reflectivity increases with increasing pressure from 15 GPa and becomes remarkably high around 20 GPa. The spectra do not show any changes from 30 GPa. From these results, we conclude that the phase transition of  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$  at room temperature starts around 15 GPa and is completed around 30 GPa and that the high-pressure phase is not a band-overlapping semimetal but a true metal.

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## I. INTRODUCTION

The Mott-type magnetic semiconductor  $\alpha$ -MnS possesses a NaCl-type face-centered cubic (B1) lattice which undergoes a rhombohedral distortion along the cube diagonal in the (111) plane with decreasing temperature. An antiferro-paramagnetic phase transition occurs at  $T_N = 150$  K. In the paramagnetic phase,  $\alpha$ -MnS is a p-type semiconductor with an activation energy  $E = 0.3$  eV and shows a metallic transition at 23 - 29 GPa [1-3]. In 1999, colossal negative magnetoresistance was observed in the (MnS)-(FeS) solid solution system [4] and many studies have been performed since then [5-11]. However the mechanism of the colossal magnetoresistance (CMR) of this system has not been clarified. Since the phenomenon is remarkable, especially at the metallic side near the metal-semiconductor phase boundary, the elucidation of the CMR is very important if the metallic

transition is to be studied in detail. The application of high pressure is a method that can be used to metalize an insulator, and in contrast with atomic doping, it enables a transition without introduction of an unnecessary complexity due to impurities. However, most metallizations of this system have previously been realized by atomic doping, so high-pressure data are very rare. We studied the pressure-induced phase transition of semiconducting sample  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$  by using X-ray diffraction (XRD) and infrared (IR) reflection measurements at room temperature.

## II. EXPERIMENTS

Polycrystalline  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  was synthesized from pure elements of iron, manganese and sulfur in evacuated quartz ampoules by annealing at 960 °C for 10 days. The ingot was sliced and polished, and the atomic composition was examined by using an X-ray fluorescence

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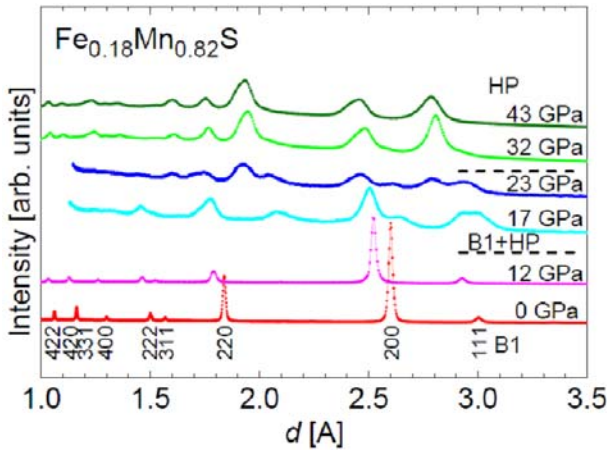


Fig. 1. (Color online) Powder X-ray diffraction patterns at various pressures for  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$ .

analysis. The  $x$ -value was obtained as  $0.18 \pm 0.01$ . The sample was powdered carefully, and XRD and IR reflection measurements were carried out under various pressures at room temperature.

The powder XRD measurement at high pressure was performed by using a diamond anvil cell (DAC) with anvils having a culet of 300  $\mu\text{m}$  in diameter and a 4:1 mixture of methanol and ethanol as a pressure-transmitting medium. The pressure was determined by using the ruby fluorescence method. The incident beam was obtained from an 18kW rotating anode X-ray generator with a Mo target fitted with a graphite monochromator (model ULTRA-X18, Rigaku corporation). The angle-dispersive diffractions were detected by using an imaging plate.

In the optical measurement, the powdered sample was squeezed into the gasket hole of the diamond anvil cell (DAC) together with a small ruby tip as a pressure monitor and was compressed preliminary to make the contact between the sample and the anvil diamond perfect. After the pressure had been released, the pressure study was started by re-compression. That is, the sample was pressurized directly without a pressure medium, which enabled us to detect the light reflected from the sample-diamond interface ( $I_{s-d}$ ) without any disturbances due to the pressure medium. The  $I_{s-d}$  spectrum was measured utilizing a Fourier transform infrared spectrometer (FT/IR-610 (JASCO)) combined with an IR microscope installed with two mirror objectives (10X) and a HgCdTe (MCT) detector. The reflectivity,  $R_{s-d}$ , was obtained from the relation  $R_{s-d} = 0.98^*(I_{s-d}/I_{g-d})$ , where the background  $I_{g-d}$  is the light reflected at the gold-diamond interface and 0.98 is the IR reflectivity of gold.

### III. RESULTS AND DISCUSSION

The powder XRD pattern of  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  ( $x = 0.18$ ) (Fig. 1) at ambient pressure shows that the crystal

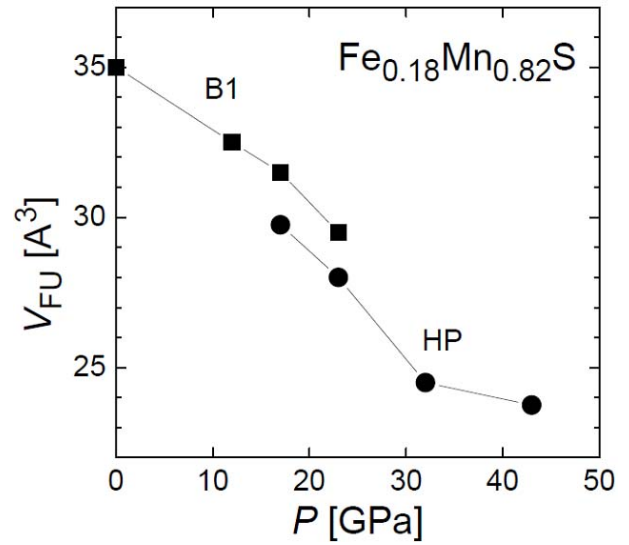


Fig. 2. Volume per formula-unit,  $V_{FU}$ , of  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$  as a function of pressure. The  $V_{FU}$  for the high-pressure phase was estimated by assuming the structure reported for the high-temperature, high-pressure phase of FeS [13].

structure is B1, the same as the mother material - MnS. The substitution of iron for manganese causes the lattice-constant to decrease from 5.22 Å to 5.19 Å, which roughly corresponds to the value extrapolated at a substitution concentration  $x$  of 0.18 from Vegard's law by assuming that the ionic radius of iron is 6% smaller than that of manganese in a di-cationic state with a coordination number of 6 [12]. This structure continues up to 12 GPa. Some new diffraction peaks appeared at pressures above 17 GPa, suggesting a structural phase transition. The peaks from the low-pressure B1 structure remained up to 23 GPa and disappeared at higher pressures above 32 GPa. The crystal structure of the high-pressure (HP) phase could not be determined clearly because of the poor quality of the data (Fig. 1). The diffraction pattern did not correspond to those expected for some possible crystal structures, for example, B2 (CsCl-type), B8 (NiAs-type), B16 (GeS-type), which are known to exist in metal-pnictides, metal-chalcogenides, and halides. The data are for the  $d$ -spacings at the HP phase are similar to those reported for -MnS at pressures higher than 26 GPa [1], but the correspondence could not be confirmed. The most likely structure is B31 (MnP-type), which is reported for FeS at temperatures higher than 420 K at atmospheric pressure or at pressures higher than 3.4 GPa at room temperature [13]. The diffraction peaks obtained at high pressures were so broadened that atomic positions could not be determined, only the lattice constants were calculated by assuming the same structure as that proposed for the FeS high-pressure phase by King and Prewitt [13].

The volume per formula unit,  $V_{FU}$ , is plotted as a function of pressure in Fig. 2. The volume of the low-pressure B1 phase initially decreases with a bulk modulus

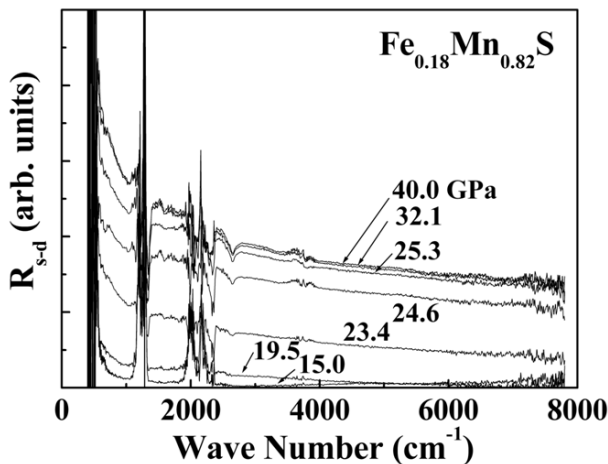


Fig. 3. Reflectivity spectra under various pressure conditions.

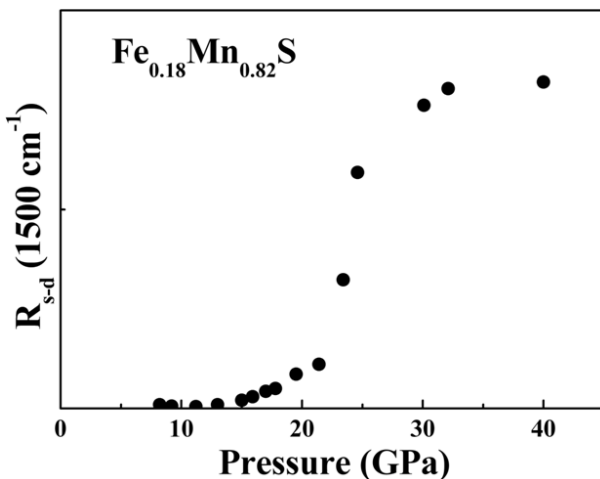


Fig. 4. Pressure dependence of the reflectivity monitored at  $1500\text{ cm}^{-1}$ .

$-dP/d\ln V = 170\text{ GPa}$ , which is almost twice that for  $\alpha\text{-MnS}$  [14]. The  $V_{FU}$  of the HP phase is 5% smaller than that of the B1 phase. The B31 structure is related to a close-packed hexagonal structure. Thus, the structural phase transition from B1 to B31 is based on a change from an fcc ABC- to an hcp AB-stacking structure. The 5% shrinkage may be associated with an overlapping in the electronic orbits and may provide the metallization mentioned later.

The IR reflection spectra of the powdered sample obtained under various pressures are shown in Fig. 3, and their pressure dependence monitored at  $1500\text{ cm}^{-1}$  is illustrated in Fig. 4. The IR reflectivity increases around 15 GPa, which is lower than that of pure MnS [2]. The increase in the IR reflectivity becomes remarkably high around 22 GPa. This suggests that a phase transition accompanied by a drastic increase in the number of free carriers starts around this pressure, which coincides with the result of the structural analysis. The

spectra do not show any changes at pressures above 30 GPa. If the increase in the number of carriers comes from a semimetallic band overlapping, the reflectivity should increase gradually with increasing pressure without saturation. The insensitivity of the reflectivity to pressure at pressures above 30 GPa suggests that the formation of a new metallic band has been completed. Therefore, the high-pressure phase of  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$ , which appears at pressures above 15 GPa, is not a band-overlapping semimetallic phase, but a true metallic phase. The gradual increasing in the reflectivity suggests that the metallic transition does not occur at once, but gradually with increasing metallic component, which coincides with the result of the X-ray structural analysis.

#### IV. CONCLUSION

XRD and IR reflection measurements were performed on  $\text{Fe}_{0.18}\text{Mn}_{0.82}\text{S}$  under various pressure conditions at room temperature. The sample was observed to start a phase transition from a semiconducting B1 phase to a metallic high-pressure phase around 15 GPa and to complete around 30 GPa. The crystal structure of the high-pressure phase could not be determined.

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