

## On the nature of the carriers in ferromagnetic FeSe

X. J. Wu

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

D. Z. Shen, Z. Z. Zhang, J. Y. Zhang,<sup>a)</sup> K. W. Liu, B. H. Li, Y. M. Lu, B. Yao, D. X. Zhao, B. S. Li, C. X. Shan, and X. W. Fan

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

H. J. Liu

Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

C. L. Yang

Institution for Optoelectric and Functional Composite Materials, School of Physics and Engineering, Sun Yat-sen University, Guang Zhou 510275, People's Republic of China

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The optical and electrical properties of FeSe thin films are studied by both optical absorption and Hall measurements, which suggest that ferromagnetic FeSe is a metal instead of a semiconductor. No absorption gap is observed in the whole spectrum range from far infrared to ultraviolet. Temperature dependent transport measurement indicates that FeSe has a resistivity about  $10^{-3} \Omega \text{ cm}$ . It is also found that there is a transition from *n*-type conductivity at low temperatures to *p*-type conductivity at higher temperatures in FeSe, which is attributed to the two-carrier transport nature and the thermal activation of localized carriers in the thin film. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712497]

As a rising field, spintronics using quantum information of spin has attracted more and more interest.<sup>1,2</sup> Spin generation and spin injection are still hot topics in achieving real spintronic devices. Ferromagnetic materials start to show significant worth in many applications, such as spin transistors, magnetoresistant devices, and quantum computation devices.

Iron selenides, which are ferromagnetic with Curie temperatures higher than 300 K, attracted more attention since they can be epitaxially grown on normal semiconductors such as ZnSe, Si, and GaAs. Bulk Fe<sub>7</sub>Se<sub>8</sub> and Fe<sub>3</sub>Se<sub>4</sub>, of which the lattice structure is NiAs type with ordered Fe vacancies, have shown Curie temperatures of 314 and 455 K, respectively.<sup>3,4</sup> Most interestingly, FeSe is claimed to be a semiconductor with a band gap of either 3.0 (Refs. 5 and 6) or 0.14 eV,<sup>7</sup> though no enough convincing experimental evidences are available. However, FeSe usually shows low resistivity in electric measurements with high carrier concentration<sup>5</sup> just like metal. Whether FeSe has a metal or a semiconductor nature is still undetermined, which remains to be an important issue since ferromagnetic semiconductors are still believed to be the first choice for spin injection in the next generation spintronic devices.

In this letter, the optical and electrical properties of tetragonal FeSe thin film were studied, which supported that FeSe is a metal-like material. A conduction reversion from *n*- to *p* type with the increase of temperature was observed and attributed to the activation of localized holes.

FeSe thin films were grown by low-pressure metal organic chemical vapor deposition (MOCVD) at 350 °C

with a chamber pressure at about  $2 \times 10^4$  Pa. To measure the electrical properties and absorption spectra conveniently, *c*-plane sapphire, which is insulating and transparent, was selected as the substrate. Iron pentacarbonyl [Fe(CO)<sub>5</sub>] and H<sub>2</sub>Se were used as precursors, flow rates of which were fixed at  $4.08 \times 10^{-6}$  and  $4.99 \times 10^{-5}$  mol/min by separate mass-flow controllers, respectively. High purity hydrogen (99.999%) was used as carrier gas with a total flow rate of 1.9 l/min. The thickness of samples is about 2 μm, which is measured by scanning electron microscopy.

Although there is sizable mismatch between tetragonal FeSe and sapphire, x-ray diffraction (not shown here) measurements show that the thin film was well oriented along the (001) direction. X-ray photoemission spectra (XPS) indicate that there is no Fe<sup>3+</sup> related signal in the film. The Fe/Se ratio is determined to be almost 1 within the error of the XPS element analysis.

Figure 1(a) shows the room temperature *M-H* curves of the FeSe sample for the in-plane and out-of-plane magnetic fields. It clearly indicates that the FeSe thin film is ferromagnetic at room temperature with in-plane easy axis. The saturation magnetization (*M<sub>s</sub>*) and the coercive force (*H<sub>c</sub>*) are about 60 emu/cc and 392 Oe for the in-plane case and are 18 emu/cc and 556 Oe for the out-of-plane case, respectively.

To better understand the carrier properties of FeSe, we studied the electrical properties of the thin film using a 7707 Hall measurement system (from Lake Shore) in the Van der Pauw configuration working at a magnetic field of 0.9 T. From the temperature dependent resistivity in Fig. 1(b), we found that the resistivity of FeSe generally decreases with the decrease of temperature, which shows a metallic conducting behavior. When the temperature is higher than

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: zhangjy53@yahoo.com.cn

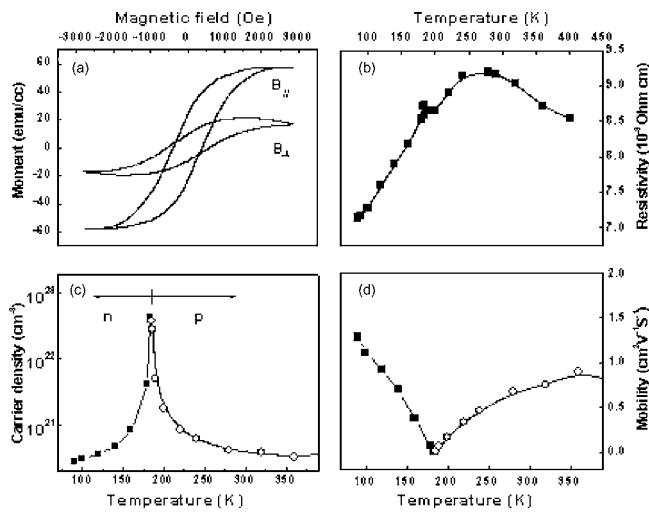


FIG. 1. (a) Room temperature  $M$ - $H$  curves of the FeSe thin film measured by vibrating-sample magnetometer with the in-plane or out-of-plane magnetic fields, as indicated. [(b)–(d)] Temperature dependent resistivity, carrier concentration, and Hall mobility in FeSe. There is a transition from  $n$ - to  $p$ -type conduction at temperature of about 185 K.

300 K, the resistivity decreases with the increase of temperature, which could originate from the thermal excited carriers and/or the two-carrier transport, as discussed later. Spin related scattering may also contribute.

Most interestingly, we found that the Hall resistivity of the FeSe thin film is dominated by electrons at low temperatures, while it is dominated by holes at high temperatures. Figures 1(c) and 1(d) are the temperature dependent carrier density and mobility of the FeSe thin film determined by normal Hall measurement, respectively. The FeSe film shows  $n$ -type Hall conductivity when the temperature is below 185 K and  $p$ -type Hall conductivity at temperatures above 185 K. We have confirmed that this carrier reversion is not induced by any structural or magnetic phase transition, confirmed by the temperature dependent x-ray diffraction (XRD) and magnetization measurement. It has long been known that the Hall resistivity of ferromagnets consists of both the ordinary and the anomalous Hall coefficients. In our FeSe sample, the anomalous Hall effect is found to be important when the magnetic field is smaller than 0.3 T and gives slight nonlinearity to the Hall resistivity at low fields. The Hall resistivity varies linearly versus the magnetic field at all temperatures when we scan the field from 0.3 to 1.6 T. Since the carrier concentrations determined by the slopes of the Hall resistivity at low and high fields do not have a large difference (within a factor of 2), we believe that the Hall data measured at 0.9 T give a good and reliable estimation of the carrier density though more accurate data could only be obtained by extracting the Hall resistivity data at much higher fields. We attribute the observed  $n$ -type to  $p$ -type conductivity reversion versus temperature to a two-carrier transport nature for the FeSe thin film. Considering the different temperature dependences of the mobility and density for holes and electrons, the transport of semiconductors or metals could be dominated by either electrons or holes at different temperatures, for which MnAs (Ref. 8) is a good example. It should be noted that the Hall measurements only offer apparent results for the two-carrier transport, except that either of the carriers dominates the conduction mightily.<sup>9</sup> The two-carrier transport nature for FeSe is further supported by our

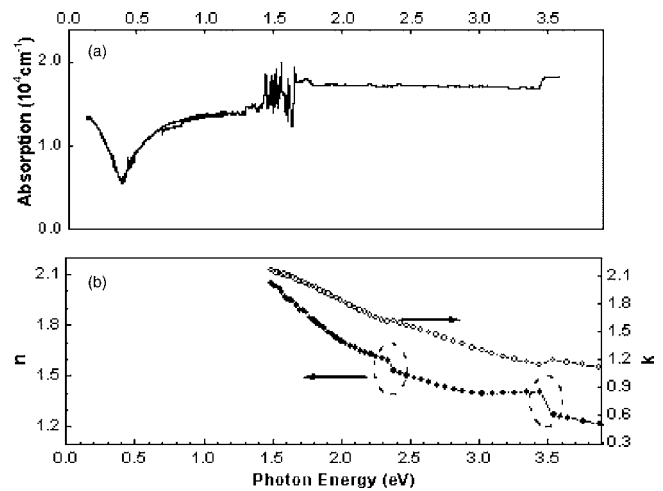


FIG. 2. (a) Absorption spectrum of the FeSe sample taken at room temperature from far infrared to ultraviolet region and (b) measured real part  $n$  and imaginary part  $k$  of the refractive index of the thin film.

theoretical calculation of its energy bands, which will be discussed later.

To get more insights on the electronic structure of FeSe, we have measured the absorption spectrum of the thin film which looks dark gray, as shown in Fig. 2(a). Firstly, we can clearly find that there is no optical gap in the whole spectrum range from far infrared to ultraviolet. The large absorption coefficient and the absence of a forbidden band suggest that FeSe is a metal instead of a semiconductor, which is also in agreement with the transport measurements and the theoretical prediction. Besides the signal fluctuation at 1.5 eV coming from the change of light source, two absorption features located at 0.4 and 3.4 eV could be resolved. The drop of the absorption as the photon energy is less than 0.4 eV is believed to come from the phonon-aided intraband absorption (Drude absorption).<sup>10</sup> It is a characteristic of the metallic absorption and can often be fitted roughly using  $1/E^2$ . As the photon goes above 0.4 eV, the absorption increases again since the interband absorption starts to dominate because of its increasing density of states. Shown in Fig. 2(b) is the measured real part  $n$  and imaginary part  $k$  of the refractive index for the FeSe thin film. We can find that there are two resonant energies at 2.3 and 3.4 eV in the  $n$  and  $k$  spectra, respectively. For the 3.4 eV point, it is in good agreement with the feature observed in the absorption spectrum. Previously, we have found that the magnetic circular dichroism (MCD) spectrum<sup>5</sup> of FeSe is dominated by a negative peak at 2.05 eV and a positive peak at 3.1 eV. We believe that the critical energy points observed in the refractive index spectrum are responsible for the measured MCD signal, though a more detailed analysis of the band structure is still needed to clarify the origin of the states. The measured refractive index  $n$ , showing monotonic decrease with the increase of photon energy, also does not support the possible semiconductor origin for FeSe. The refractive index of semiconductor will always increase with the increase of photon energy, though it will be with complicated response when the photon energy approaches or is higher than some von Hove singularities.

The two-carrier transport model for the FeSe thin film is supported by our calculated band structure using density functional theory within the local density approximation.<sup>11–13</sup> The lattice constant obtained by the XRD data with an anti-PbO structure was used as the input parameters for the the-

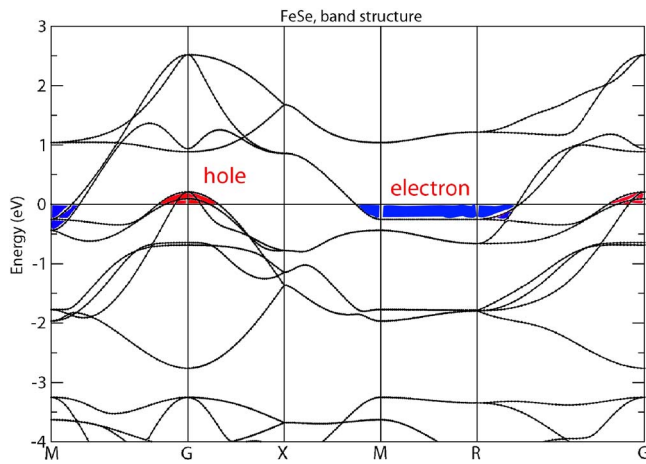


FIG. 3. (Color online) Calculated band structure of FeSe using density functional theory within the local density approximation. The Fermi level is at  $E=0$ . The hole and electron bands are marked for clarity.

oretical modeling. The calculated electronic structure of FeSe is shown in Fig. 3. It shows that the stoichiometric FeSe is a metal without any energy gap, which is in agreement with both the optical and transport measurements. The valence electrons of FeSe will be filled up to the Fermi level at 0 eV. Clearly, we can find that FeSe contains both holes (peak  $G$ , marked in red) with positive effective mass and electrons ( $M$  and  $R$  valleys, marked in blue) and with negative effective mass near the Fermi level, both of which will contribute to the electrical conductivity. This band structure really shows that there are two kinds of carriers in this system. From the experiment, we know that the electrons dominate the Hall resistivity at low temperatures, which suggests that there are more electrons than holes at low temperatures since the mobility of most of the electrons seems to be smaller than that of holes from the band structure. At higher temperatures, there is a reversion from  $n$  to  $p$  type for the thin film and the holes contribute more in the electrical conductivity. The reversion could partly come from the different temperature dependences of mobility for electrons and holes, which is still unknown at present in this material. Most importantly, we believe that the reversion originates from the increased hole density which is derived from both the band structure and the thermal activated acceptors. Due to thermal excitation with the increase of temperature, more electrons will be excited from the Fermi level to higher electronic states. Then, more holes will be created near  $G$  points and

more electrons will relax to  $M$  ( $R$ ) valleys. From the flat dispersion for the curves at  $M$  ( $R$ ) valleys, we know that most of the electrons at those states have very large effective mass and thus very small mobility. However, the hole states near  $G$  points have smaller effective mass and thus much larger mobility. Furthermore, the thermal activation of acceptors introduced by slight off stoichiometry in the thin film will also result in a significant change of the hole density, which is evidenced by the large change of carrier concentration upon change of growth parameters. So the observed reversal in the Hall resistance could be well understood using the two-carrier transport model based on the calculated band structure of FeSe.

In conclusion, we have measured the optical, electrical, and magnetic properties of MOCVD grown FeSe thin film. It is found that FeSe is a ferromagnetic metal with Curie temperatures higher than 300 K. The conversion of conduction type from  $n$  to  $p$  was observed with increasing temperature. This provides an opportunity to inject spins by either holes or electrons using the same material. The theoretical calculation indicates that FeSe is a metal with double carriers, which well explains the observed transport properties.

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