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Metal–Insulator Transition Induced by Spin Reorientation in Fe_7Se_8 Grain BoundariesGuowei Li,[†] Baomin Zhang,[‡] Tigran Baluyan,[§] Jiancun Rao,^{||} Jiquan Wu,[†] Alla A. Novakova,[§] Petra Rudolf,[†] Graeme R. Blake,[†] Robert A. de Groot,^{†,⊥} and Thomas T. M. Palstra^{*,†,⊥}[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands[‡]School of Physics and Technology, University of Jinan, 336 West Road of Nan Xinzhuang, 250022 Jinan, P. R. China[§]Faculty of Physics, Moscow State University, Vorobyovy Gory, 119899 Moscow, Russia^{||}School of Materials Science and Engineering, Harbin Institute of Technology, 150001 Harbin, P. R. China[⊥]Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

S Supporting Information

ABSTRACT: Fe_7Se_8 exists as a hexagonal NiAs -like crystal structure with a large number of ordered intrinsic vacancies. It is an ideal candidate for studying the effect of defects on properties such as magnetism and electrical transport. In this work, highly crystalline Fe_7Se_8 with the 3c crystal structure was synthesized by a solid-state reaction. Sharp changes in the magnetization at 100 K confirm a rotation of the spins from the ab plane to the c axis with decreasing temperature. We observe an interesting metal–insulator transition at the same temperature as the spin-direction changes. We propose that locked spins in the grain boundaries induce electron localization and result in the metal–insulator transition. Electron localization is confirmed by X-ray photoelectron spectroscopy of the Fe 2p peaks, which exhibit two characteristic satellite peaks. This mechanism is also verified by comparing it with the properties of the 4c- Fe_7Se_8 crystal structure.

Spin-Reorientation Transitions

1. INTRODUCTION

Crystal defects, such as grain boundaries, stacking faults, dislocations, vacancies, etc., widely exist in materials. They influence properties in many aspects from electrical transport to magnetism to mechanical performance. Charge-carrier transport can provide a wealth of information on solid-state materials and is sensitive to various defects.¹ We can now grow large-scale, high-quality materials that are nearly defect-free, such as graphene films, molybdenum sulfide films, and functional nanowires. However, high-resolution transmission electron microscopy still proves that such materials can consist of several crystallites separated by domain boundaries.^{2–4} Vacancy formation of various elements is another difficult problem for materials scientists. According to thermodynamics, the formation of vacancies even in equilibrium is a corollary of entropy. Grain boundaries, in combination with vacancies, can act as scattering sites and localization centers for carriers and degrade transport via the formation of electrostatic barriers between single-crystalline domains. This effect is significantly enhanced in low-dimensional materials such as thin films as a result of limited phase space and reduction in Coulomb screening.⁵ In addition, the charge-carrier mobility is strongly dependent on the shape and size of the boundaries and the form of the vacancies, i.e., whether they are isolated or in clusters.⁶ This makes a clear understanding of the electrical transport mechanism more complicated and poses limits for applications as high-conductivity electrode materials for

batteries, modern spintronic devices, and highly efficient photocatalysts.

Nevertheless, defects are not generally detrimental to the materials' properties and application performance. Magneto-resistance (MR) effects, which have been exploited in magnetic field sensors, offer a research prototype for exploring the influence of defects. Colossal MR in single-crystal samples is a result of a metal–insulator transition with suppression of spin fluctuations due to double exchange. However, in polycrystalline samples that include various defects, MR is dominated by spin-polarized tunneling across grain boundaries.⁷ A spin-valve system based on this principle was fabricated by growing Fe_3O_4 epitaxially on a MgO substrate. By application of a small magnetic field, the electron conduction could be modified across the antiphase boundaries. The MR effect based on a single boundary is expected to be much larger.⁸ In addition, defect engineering is a powerful tool to create magnetic moments in materials. Defects can be introduced more easily at the surface than in bulk because fewer bonds have to be broken. Therefore, in low-dimensional or nanostructured crystals, where the surface-to-volume ratio is much larger than that in macroscopic crystals, defects constitute a larger fraction and can efficiently control the properties.⁹ For example, it is reported that localized electrons at graphene boundaries can create a net

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magnetization. These magnetic states can further induce dispersionless flat bands near the Fermi energy. These flat bands can be accessed by a small doping concentration, leading to enhanced magnetism.¹⁰ Magnetism can also be created and manipulated by adatoms, vacancies, or zigzag edges.^{11,12} Defects also play an important role in preparing materials for oxygen reduction, lithium-ion batteries, solar cells, etc.^{13,14} Thus, a deep understanding of the way that defects influence the material properties is the first step toward the successful design of advanced functional materials that meet the requirements of various devices and applications.

Fe_7Se_8 exists as a hexagonal NiAs-like structure with an ordered distribution of Fe vacancies, which makes it an ideal compound for studying the effect of defects on various properties including magnetization and electrical transport. Depending on the synthesis method, Fe_7Se_8 can be formed in two different superstructures. Furnace cooling (cooling to room temperature in the furnace) from the reaction temperature results in the 4c structure, where the unit cell length along the *c* axis is 4 times larger than that of the fundamental NiAs-type cell.¹⁵ Quenching from temperatures above 400 °C produces the 3c structure with a *c* axis 3 times larger than that of NiAs. A typical unit cell for the 3c structure is shown in Figure 1. The

Figure 1. Unit cell for a 3c- Fe_7Se_8 superstructure, where black circles represent Fe atoms, open circles represent Fe vacancies, and Se atoms are omitted for clarity. A, B, and C represent the three nonequivalent Fe sites (atoms to the right of the label) as proven by Mössbauer spectroscopy.

ordered appearance of Fe vacancies in every second layer results in the superstructure. Neutron diffraction studies indicate that the Fe moments are arranged parallel in the same layer but are antiparallel to the moments in the adjacent layer. This arrangement results in a net magnetic moment, where the ferrimagnetic behavior is a direct consequence of the existence of vacancies.^{15,16} Further studies revealed that the magnetic moments lie in the *ab* plane for both the 3c and 4c structures. However, decreasing the temperature leads to an abrupt change in the direction of the moments toward the *c* axis in the 3c structure.¹⁵ For the 4c structure, this change happens over a wide temperature range between 100 and 220 K.

However, the exact transition temperatures depend on the detailed synthesis procedure.¹⁷ Resistivity measurements on the single-crystalline 3c structure indicate that it is a good metal with no anomalous resistivity.¹⁸ Another study showed that the temperature-dependent resistivity along different axes exhibits different behavior. Below the spin rotation temperature, both the 3c and 4c structures show metallic conductivity, while above the transition temperature, the resistivity is nearly temperature-independent.¹⁹ Unfortunately, no detailed explanation exists for these interesting resistivity anomalies.

In this work, high-purity samples with the 3c structure of Fe_7Se_8 were synthesized by a solid-state reaction method. The electrical resistivity and magnetization properties were investigated systematically. We found an interesting metal–insulator transition at the same temperature as that for the change in the spin direction. We propose that locked spins in the grain boundaries induce electron localization, resulting in the metal–insulator transition. This electron localization was confirmed by X-ray photoelectron spectroscopy, where two distinct Fe 2p satellite peaks were observed. The proposed mechanism was verified by a comparison with the properties of the 4c- Fe_7Se_8 structure.

2. EXPERIMENTAL SECTION

2.1. Synthesis. Polycrystalline samples were synthesized by a solid-state reaction method. In a typical synthesis procedure, high-purity (99.999%) powders of Fe (0.1710 g) and Se (0.2764 g) were mixed together according to the chemical ratio of Fe_7Se_8 . The mixture was ground thoroughly, transferred to an evacuated quartz tube, and then sintered in a muffle furnace. The furnace was first heated at a rate of 2.5 °C/min to 600 °C for 48 h, then to 900 °C in 1 h and kept for 24 h, and to 1050 °C in 0.5 h and kept for 2 h. The sample was cooled in the furnace to room temperature in about 20 h. The resulting powder was ground, pelletized, and sealed again in an evacuated quartz tube. The tube was placed in the furnace, heated to 700 °C in 4 h, and kept at this temperature for 48 h. The sample was then cooled in the furnace to 400 °C naturally in 2 h. Finally, the tube was quenched in water when the temperature reached 400 °C. For the synthesis of a sample with 4c structure, all procedures were kept the same except the final step. The sample was cooled to room temperature naturally from 700 °C by switching off the furnace in 15 h.

2.2. Characterization. Room temperature powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer equipped with a Cu $K\alpha$ source ($\lambda = 0.15406$ nm). Rietveld refinements of the diffraction data were performed using the GSAS and EXPGUI suite of programs. The morphology and crystal structure were probed using scanning electron microscopy (SEM; Philips XL 30). High-resolution transmission electron microscopy (HRTEM) and TEM–energy-dispersive X-ray spectroscopy were performed using a Tecnai G2 F30 S-Twin at an acceleration voltage of 300 kV. The magnetization was measured using a Quantum Design MPMS-XL7 SQUID magnetometer. For measurement of the electrical properties, a circular-shaped polycrystalline sample was prepared by pressing the powder under 1500 MPa (3 tons) for 15 min. The electrical contacts were made using a gold wire of 0.01 mm diameter connected to the sample with silver paint. The electrical measurements were performed using a Quantum Design Physical Properties Measurement System equipped with a SR830 DSP lock-in amplifier (Stanford Research Systems). Mössbauer spectra were measured at room temperature and in the temperature interval of 80–110 K, using a MS-1104 M constant acceleration spectrometer with a $^{57}\text{Co}(\text{Rh})$ radiation source. X-ray photoelectron spectroscopy (XPS) data were collected using a Surface Science SSX-100 ESCA instrument equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) and operating at a base pressure of 1×10^{-9} mbar. The spectra were recorded with an electron takeoff angle of 37° with respect to the surface normal on at least three different spots with a diameter of 1000

μm to check for reproducibility. The spectra were analyzed using the least-squares curve-fitting program *Winspec* developed at the LISE laboratory, University of Namur, Namur, Belgium. The binding energies are given as ± 0.1 eV and referenced to the C 1s photoemission peak, centered at 284.8 eV.

3. RESULTS AND DISCUSSION

3.1. Phase and Morphology. Figure 2 displays the XRD pattern of the as-synthesized sample. It is consistent with the

Figure 2. Experimental powder XRD data and Rietveld refinement of the as-synthesized Fe_7Se_8 sample at 300 K. The inset shows the pattern near 15° .

hexagonal $3c\text{-Fe}_7\text{Se}_8$ phase (JCPDS 48-1451). Rietveld refinement was performed based on the reported $P3_1$ structural model, with lattice parameters at 300 K of $a = b = 0.7241(4)$ nm and $c = 1.7613(5)$ nm. The obtained cell parameters are derived from the basic NiAs-type cell by doubling the a and b axes and tripling the c axis. The observation of the 003 peak at $2\theta = 15.1^\circ$ indicates vacancies at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{3})$, and $(0, \frac{1}{2}, \frac{2}{3})$. They appear on every second Fe layer, which agrees with earlier neutron diffraction results on a single-crystal sample.¹⁵ The final agreement factors converged to $R_p = 0.0229$ and $wR_p = 0.0205$. No peaks belonging to impurity phases of other iron selenide compounds such as Fe_3Se_4 , FeSe_2 , or FeSe were observed. SEM images in Figure S1 indicate that the product mainly consists of irregular particles up to 100 nm in size. However, one can also clearly see the existence of small particles of nanometer size. Elemental analysis on different areas shows similar Fe/Se ratios, always very close to stoichiometric Fe_7Se_8 . This also confirms the high purity of the investigated sample in this work.

3.2. Electrical Transport. Alternating-current electrical resistivity of the polycrystalline Fe_7Se_8 sample was measured by a standard four-probe method from room temperature to 5 K. Figure 3a shows the temperature dependence of the electrical resistivity. The inset provides a magnified plot below 100 K. In the temperature range between 30 and 100 K, the sample shows metallic behavior, characterized by an increase of the resistivity with temperature, even though the value is larger than the unitary scattering limit. This is in accordance with a previous measurement on a bulk single-crystalline sample¹⁸ and further confirmed by our theoretical calculations (see Figure 5), which show that the majority spin states for all Fe atoms are almost completely occupied, while the minority spin states are partially filled.

The hybridization between the Fe and Se 4p states is also relatively weak. However, the resistivity is ~ 82 m $\Omega\cdot\text{cm}$ in the metallic regime, which is significantly larger than the value for a

Figure 3. (a) Temperature dependence of the electrical resistivity of polycrystalline Fe_7Se_8 . The inset details the behavior below 100 K. (b) SEM image of the pellet for resistivity measurements.

conventional metal (generally $\ll 1$ m $\Omega\cdot\text{cm}$). One possibility for the large resistivity is the existence of Fe vacancy clusters. As discussed in the Introduction, one pronounced difference between Fe_7Se_8 and other ordinary sp^3 -bonded compounds is the facile realization of a high degree of disorder caused by rapid quenching from high temperature during synthesis. These Fe vacancy clusters, in combination with ordered, single isolated defects, can create insulating hole states in the band gap, resulting in large electron scattering and localization, small mobilities, and thus increased resistivity. This effect is enhanced because of the strong directionality of the resonant p bonds that makes the overlap more sensitive to distortions, like in the phase change material GeSb_2Te_4 .¹ As further evidence, the carrier densities are lower than expected if one assumes a single isolated defect.²⁰ First-principle calculations have confirmed electron localization on such vacancy clusters.²¹ Interestingly, it was found that single-crystalline Fe_7Se_8 grown with the Bridgman method showed a much larger resistivity than samples grown by chemical transport. This can be attributed to fewer imperfections formed in the latter strategy.¹⁸ The second reason for the high resistivity is the microstructure within the pellet. As we can see from SEM images (see, for example, Figure 3b), even if the pellet is pressed at a high pressure, one can clearly still observe the interconnected porosity. The large amount of open space due to intragranular pores hinders the formation of a dense microstructure and contributes significantly to the resistivity. Sintering at high temperature can increase the grain size and favor the formation of a dense sample, with a one order of magnitude lower resistivity.^{22,23} Unfortunately, the synthesis of the $3c\text{-Fe}_7\text{Se}_8$ phase requires quenching from high temperature. This results in a fragile pellet, which is not easy to handle in resistivity measurements. In addition, a high sintering temperature can also result in the formation of other impurity phases, such as Fe_3Se_4 and FeSe_2 .

With decreasing temperature, a resistivity upturn is observed below 25 K, as shown in the inset of Figure 3b. This upturn is enhanced by applying a magnetic field, as we can see from

Figure 4a. The appearance of a resistivity minimum is a generic feature of ferromagnetic granular materials.

Figure 4. (a) Temperature dependence of the resistivity of Fe_7Se_8 at low temperature. An upturn of the resistivity is observed for different magnetic fields. (b) Fit for the upturn using eq 4.

Figure 5. Total DOS of pure Fe_7Se_8 with the hexagonal 3c structure. The red line stands for spin-up, while the black line stands for spin-down.

Various explanations have been proposed such as a Coulomb blockade, weak electron localization, the Kondo effect, and spin-dependent scattering (spin-polarized tunneling) through the grain boundaries. Spin-dependent scattering is known to be a general characteristic of polycrystalline samples.²⁴ In this model, the temperature dependence of the resistivity can be expressed as

$$\rho = \rho_0 + \rho_s \ln(T) \quad (1)$$

where ρ_0 is the residual resistivity and ρ_s is the spin-dependent scattering resistivity. A fit to our data with the above model appears reasonable, but a negative coefficient for the spin-dependent scattering resistivity is extracted, which is physically meaningless. Indeed, this mechanism is unrealistic because, at such a low temperature, the motion of spin-polarized carriers is strongly confined. The tunneling of conduction electrons between the antiferromagnetically coupled grain boundaries is blocked. A second possible explanation, the Kondo effect, is widely observed in metals with a small concentration of magnetic impurities. The coupling between conduction

electron spins and magnetic impurity moments gives rise to a low-temperature resistivity minimum. In this model, an increasing external magnetic field should suppress the resistivity minimum and completely disappears for large fields.²⁴ Obviously, this is in contradiction with our results: increasing the field lowers the minimum in resistivity, which is most pronounced in our maximum applied field of 4 T. Considering the polycrystalline nature and high porosity of the investigated sample, it is necessary to analyze the effect of bulk scattering. In this case, the resistivity can be written as

$$\rho = \rho_{\text{el}} + \rho_{\text{in}} \quad (2)$$

where ρ_{el} represents the contributions from elastic processes [Coulomb interactions (CI)] and ρ_{in} represents those from inelastic processes [electron–electron (e–e) interactions]. It has been reported that a decrease in the mean-free path of electrons will lead to multiple elastic scatterings from site to site in disordered materials. In this case, e–e interactions are responsible for the upturn in the resistivity because of strong correlation effects. In the elastic e–e interaction picture, the resistivity is given by

$$\rho = \rho_0 - \rho_{\text{el}} T^{1/2} \quad (3)$$

where ρ_0 is the residual resistivity contributed by temperature-independent scattering processes and ρ_{el} is a constant. All of the other temperature-dependent inelastic scattering processes, such as electron–phonon and electron–magnon scattering, are described by a general power law as T^n . Thus, the total resistivity of the system can be described as²⁴

$$\rho = \rho_0 - \rho_{\text{el}} T^{1/2} + \rho_{\text{in}} T^n \quad (4)$$

The results of the corresponding fits are presented in Figure 4b. One can see excellent agreement between the experimental data and fitted curves. Therefore, we conclude that the upturn in resistivity at low temperature is the result of competition between elastic e–e interactions and inelastic processes. The magnetic field dependence of the resistivity provides more evidence for the validity of the above model. Our results are different from the previously reported resistivity minima, where a significant change in the resistivity can be obtained with different applied fields (up to 42% with a field of 8 T in neodymium-based manganites,²⁵ and 200% at 5 T in manganese perovskites²⁶). In our case, the resistivity only decreases by 0.5% in a field of 4 T. Aleiner et al.²⁷ considered a quantum correction to the electrical conductivity due to the influence of an external magnetic field. Here $\sigma_{\text{el}}(T, H) = \sigma_0 + \delta\sigma_{\text{CI}}(T, H) + \delta\sigma_{\text{DP}}(T, H)$, where $\delta\sigma_{\text{CI}}(T, H)$ is the CI contribution in a nonzero magnetic field and $\delta\sigma_{\text{DP}}(T, H)$ is the contribution of dephasing caused by both the magnetic field and CI. Assuming a parabolic spectrum and full spin polarization of the carriers, we can expect $\delta\sigma_{\text{CI}}(T, H) \gg \delta\sigma_{\text{DP}}(T, H)$.²⁸ Thus, the bulk scattering model predicts a weak magnetic field dependence of the resistivity when quantum effects are considered, consistent with our experimental results. The corresponding fitting coefficients (ρ_{el} and ρ_{in}) are of the same order of magnitude and do not change significantly from 0.005 to 4 T because of the weak magnetic field dependence of the e–e interaction.

Finally, we will discuss the resistivity regime above 100 K, which is the most significant aspect of this work. As we discussed above, 3c- Fe_7Se_8 is a metal, based on previous research. The decreasing resistivity with temperatures above

100 K indicates semiconductor behavior. A metal–semiconductor transition is observed in many systems. One of the most important reasons is the existence of various defects such as vacancies. These vacancies can be isolated or clustered, arranged in an ordered or a disordered fashion; each of these different types of vacancies has a significant influence on electron transport and can induce a metal–semiconductor transition.^{1,29,30} Fe_7Se_8 is particularly sensitive because of the formation of Fe vacancies. Their distribution is easily influenced by the temperature profiles during synthesis. Thus, we studied the effect of vacancies by density functional theory (DFT). The results show that pure Fe_7Se_8 is a metallic ferrimagnet, which agrees well with our experimental findings. In order to study the effect of Fe vacancies in Fe_7Se_8 on its electronic structure, DFT calculations were performed on the unit cell using the experimental lattice parameters. These calculations can be classified into two categories, represented by the cases of 5% and 10% Fe vacancies. For the case with 5% Fe vacancies (with the formula $\text{Fe}_{20}\text{Se}_{24}$), two calculations were performed on cells containing 20 Fe and 24 Se atoms, where a Fe vacancy resided in the Fe-rich layer or in the Fe-poor layer, respectively. The calculation results are shown in Figure S2. It is found that 5% Fe-vacancy Fe_7Se_8 remains metallic regardless of the occupation of Fe vacancies in the different Fe layers. For the case with 10% Fe vacancies, five calculations were carried out on cells containing 19 Fe and 24 Se atoms. The distribution of these two Fe vacancies in the unit cell have five distinct configurations: (a) the two Fe vacancies are in the same Fe-rich layer; (b) the two Fe vacancies are in the same Fe-poor layer; (c) the two Fe vacancies are in adjacent Fe-poor layers along the c direction; (d) the two Fe vacancies are in adjacent Fe-rich layers along the c direction; (e) the two Fe vacancies are in adjacent Fe-rich and Fe-poor layers along the c direction. Usually, the interaction between two vacancies separated by a longer distance has a smaller effect on the electronic structure than two vacancies separated by a shorter distance. Consequently, in each of these five calculations, we only considered the case where the two Fe vacancies are the shortest distance apart. We find that 10% Fe-vacancy Fe_7Se_8 is also metallic, regardless of the distribution of Fe vacancies in different Fe layers. Correlation effects play an important role in determining the electronic and magnetic properties of iron oxides (such as Fe_3O_4), and an empirical parameter U with a value of 3.7 eV is introduced to the DFT calculations in order to give a better description. Compared to iron oxides, the correlation effect in iron sulfides (such as Fe_3S_4) is weaker, but we still need to include correlations in the DFT calculations, and an empirical parameter U with a value of 1.0 eV is used. In order to describe the electronic and magnetic properties of Fe_7Se_8 , we should check whether the empirical parameter U should be used and whether other values of U give a better description. We know the experimental lattice parameters (7.17, 7.17, and 17.46 Å) and the total magnetization of Fe_7Se_8 (7.8 μ_{B} per $\text{Fe}_{21}\text{Se}_{24}$) at low temperature (Table S1). Therefore, we performed a series of DFT calculations where the value of U was varied from 0, 0.5, 0.9, 1.0, 1.1, 1.5, to 2.0 eV. The optimized lattice parameters and calculated total magnetization of $\text{Fe}_{21}\text{Se}_{24}$ are shown in Table S1. Thus, we find that the case where U is 1.0 eV agrees best with the experimental lattice parameters and measured total magnetization. Consequently, for all of the calculations in this manuscript, we consider the correlation effect in Fe_7Se_8 by including the parameter U with a value of 1.0 eV.

Obviously, the concentration and distribution of Fe vacancies in the unit cell are not enough to induce a metal–insulator transition in this structure. We must consider that $3c\text{-Fe}_7\text{Se}_8$ also has a magnetic transition at a similar temperature. Here, the spin direction changes from in the ab plane to the c direction when the temperature is decreased to 100–120 K. Therefore, more techniques are required to study the effect of spin rotation on electrical transport.

3.3. Magnetization Properties. The magnetic hysteresis loops at 5 and 300 K are presented in Figure 6a. Both curves

Figure 6. (a) Magnetic hysteresis loops for $3c\text{-Fe}_7\text{Se}_8$ at 300 and 5 K. (b) ZFC–FC magnetization curves measured under a magnetic field of 200 Oe. The arrows illustrate the abrupt change of the spin direction from the ab plane to the c axis at 100 K.

show typical ferromagnetic behavior with a coercivity of less than 500 Oe at all temperatures. The law of approach to saturation is widely used for modeling the magnetization curves of polycrystalline soft magnetic phases. Generally, the law is expressed as

$$M_{\text{H}} = M_{\text{S}}(1 - A/H - B/H^2) + C\sqrt{H} \quad (5)$$

where M_{S} is the spontaneous magnetization and A/H is related to structural defects within magnetic substances, which causes fluctuations of the local internal stress fields. The term B/H^2 is a measure of the magnetic anisotropy energy, and the final term is the high-field susceptibility resulting from an increase in the spontaneous magnetization.³¹ Excellent fits can be obtained with this model, as shown in the inset of Figure 6a. The saturation magnetization is determined to be 2.56 μ_{B} /f.u. (f.u. = formula units) at 5 K, in good agreement with the calculated value of 2.5 μ_{B} /f.u.³² The local moments on the three Fe sites are nearly the same, with values of 3.1, 2.8, and 3.0 μ_{B} /f.u. These values are significantly smaller than expected for an ionic model, with four and five unpaired electrons associated with Fe^{2+} and Fe^{3+} , considering spin-only contributions. The coefficient of the A/H term is accordingly found to be 187 and 249 Oe at 5 and 300 K, respectively. It has the same magnitude as that in many other materials such as single-crystalline Fe_3S_4 and Nd–Fe–B alloys.^{31,33} However, the larger

coefficient at higher temperatures is in contradiction with the common understanding of the decreasing influence of defects on the spin rotation with increasing temperature. This means that there is a larger contribution to the magnetization from the structural defects at 300 K. The coefficient for the B/H^2 term is $3.42 \times 10^4 \text{ Oe}^2$ at 5 K and $2.46 \times 10^4 \text{ Oe}^2$ at 300 K. These values are 4 orders of magnitude smaller than those in highly anisotropic ferromagnets and even smaller than those for cubic Fe_3S_4 .³¹ This indicates an easier rotation of magnetization against the magnetocrystalline anisotropy. More information is obtained from the zero-field-cooled (ZFC)–field-cooled (FC) curves, as shown in Figure 6b. The abrupt change in moment at 100 K corresponds to the change in the spin direction. The spontaneous magnetization lies in the ab plane above 100 K and is parallel to the c axis below 100 K. Interestingly, the ZFC and FC curves do not coincide even at 345 K. This implies the existence of “locked” spins that are not reversible in the warming process. The large divergence below 100 K is a result of the competition between the anisotropy energy along different directions. One favors the spin orientation along the c axis, while another favors the orientation in the ab plane. Both anisotropy energies are temperature-dependent and sensitive to the external magnetic field.¹⁷

The temperature dependence of the saturation magnetization in a field of 4 T is shown in Figure 7a. The fits indicate two

Figure 7. (a) Temperature dependence of the saturation magnetization in an applied field of 4 T. (b) Fit using a modified Bloch law with a power of 2.5.

temperature regimes: M_{SAT} increases monotonically with decreasing temperature until 100 K and then decreases below 100 K. The competition between the thermal and magnetocrystalline anisotropy energies can be responsible for this behavior. In the cooling process from high temperature, the external magnetic field is more effective in aligning the magnetic moments. This leads to an increase of M_{SAT} until 100 K. For temperatures below 100 K, the decrease in M_{SAT} with decreasing temperature is a result of the competition between the thermal and anisotropy energies. The anisotropy energy increases as the measurement temperature decreases. The applied magnetic field overcomes the anisotropy field and

results in a decreased M_{SAT} .³⁴ For a better understanding of the change in the anisotropy energy at 100 K, we fitted the temperature dependence using a spin-wave theory model. In this theory, the change in the saturation magnetization is dominated by the excitation of long-wavelength spin waves. In the linear approximation of the Bloch spin-wave theory, the magnetization is described by the formula $M_{\text{SAT}}(T) = M_0(1 - AT^n)$, where $M_{\text{SAT}}(T)$ is the saturation magnetization at a given temperature, M_0 is the magnetization of the ground state at 0 K, A is Bloch's constant, and n is the Bloch power. Assuming that all of the spins are perfectly ordered in the quasi-static approximation and have vanishingly small configurational entropy, the power $3/2$ is obtained. This is confirmed to be very accurate especially in single-crystal ferromagnets.³⁵ However, generally the Bloch “ $AT^{3/2}$ ” law gives a bad fit for experimental data. Deviations are reported for various systems. Also, other commonly used powers for nanostructures such as 1, 2, and 3 all failed to give satisfactory fits in our case, as shown in Figure 7a.³⁶ However, an excellent fit is obtained by adopting a power of $5/2$. As shown in Figure 7b, the magnetization obeys the $AT^{5/2}$ law very well, at least to 100 K ($R^2 = 0.99993$). Previous research found that the power is independent of the type of spin order.³⁷ It depends on whether the spin quantum number is integral or half-integral and on the dimensionality of the magnetic interactions. The power $5/2$ is rarely reported. It is appropriate for half-integral spin values with dominating one-dimensional axial interactions. This suggests that for temperatures above 100 K the interlayer Fe–Se–Fe bonds along the c axis dominate the superexchange in the $3\text{c-Fe}_7\text{Se}_8$ structure. The deviation from linear dependence below 100 K is the result of spin rotation at this temperature. Thus, a different power is necessary to fit the data and confirms a change to a more anisotropic interaction at low temperature.³⁸ The conduction bands are responsible for the magnetic interactions in metallic ferromagnets. They are split or shifted because of the strong internal fields. Generally, the interaction strength changes continuously with temperature, although it is usually a small effect. The moderate change in the exchange anisotropy will not influence the dimensionality of the interaction, and a constant power is obeyed in the entire temperature regime.³⁸ However, if the change in the anisotropy exceeds a threshold value, a discrete thermodynamic reaction occurs and leads to a deviation of the associated power. A thermodynamic crossover between powers as a function of the temperature is widely observed in metallic ferromagnets such as GdZn , GdAl_2 , and hcp ferromagnetic Fe.³⁹

Interesting information can be obtained from the temperature dependence of the coercive field and remanence, as shown in Figure 8a. The coercive field is nearly temperature-independent above 110 K. Thus, we can assume that all magnetic domains are fully strain-relaxed and the sample has a well-defined value of the coercive field. With decreasing temperature, the coercive field increases rapidly. A maximum coercive field is obtained at 100 K. The presence of anomalous coercivity can generally be caused by the existence of two exchange-coupled phases: a ferromagnetic phase with a reversible magnetic moment and a fixed phase with an irreversible moment such as spin-glass-like impurities. Additional local anisotropy could be created at the interface. Competition arises with the demagnetization field, which acts as an energy barrier to domain-wall motion. Exchange-bias fields can be expected for the interface phase,⁴⁰ but we do not see any shift of the hysteresis loops over the entire measured

Figure 8. (a) Temperature dependence of the remanence and coercive field. (b) HRTEM image of the sample, where the grain boundaries are highlighted by arrows.

temperature regime. We propose that the sample may include defects such as grain boundaries and stacking faults. These defects divide the crystals into small domains with rich interfacial areas (here referred to as core/shell structures). With decreasing temperature, the magnetic moment is rotated from the ab plane to the c axis, as we showed above. However, some of the moments located in the defect (shell) areas are “frozen” and can be considered as localized structural and magnetic defects. The disorder reaches a maximum when the moment in the core is fully aligned along the c axis, while the moment in the shell is still locked at 100 K. This appears to be the reason for the small difference between the ZFC and FC curves at around 100 K, as shown in Figure 6b. The coercive field below this transition is much larger and shows a linear temperature dependence. This corresponds to domains that include additional pinning centers in comparison with the state above the transition temperature. The abrupt increase in the remanence confirms the increase of the pinning centers at this temperature, as shown in Figure 7a. The HRTEM image displayed in Figure 8b clearly shows the existence of rich boundaries in the nanostructures, as highlighted by arrows.

3.4. Mössbauer Spectra. Mössbauer spectroscopy is a powerful tool to determine the magnetic structure, as well as the magnetic states, of a material. Mössbauer spectra at different temperatures (80, 110, and 120 K) were measured, and only the spectrum at 80 K is shown here (Figure 9a). Several important parameters are displayed in Table 1. It can be seen that the spectrum can be fitted well with three sextets (as for the spectra at other temperatures). Isomer shifts (δ) at 80 K in the range of 0.82–0.86 mm/s suggest the strong ferrous character of Fe at all three sites. No sextets associated with high-spin Fe^{3+} with isomer shifts in the range of 0.2–0.37 mm/s are found at any temperature.^{31,41} Thus, the 3c- Fe_7Se_8 structure cannot be explained simply by a ferrous and ferric ion model such as $Fe_2^{3+}Fe_5^{2+}Se_8^{2-}$. A pure Fe^{2+} sextet model is also excluded because of the electrical neutrality of the material.

Figure 9. (a) ^{57}Fe Mössbauer spectra of the 3c structure at 80 K. (b) Exchange interactions in the 3c structure with the NiAs unit cell.

Table 1. Hyperfine Parameters Obtained from Fitting the ^{57}Fe Mössbauer Spectra at Different Temperatures^a

T , K	site	δ , mm/s	H_{hf} kOe	H_{hf} ratio	H_{hf} per Fe–Se–Fe
80	A	0.8598	274.33	18	
	B	0.8580	226.66	14.87	15.23 ^b
	C	0.8253	202.04	13.25	15.19 ^c
100	A	0.8410	278.12	18	
	B	0.8454	224.61	14.53	15.42
	C	0.8350	192.46	12.46	15.53
110	A	0.8311	279.28	18	
	B	0.8366	221.50	14.28	15.53
	C	0.7954	190.54	12.28	15.48

^a H is the magnetic hyperfine field at the ^{57}Fe nuclei, and δ is the isomer shift relative to Fe. The calculation method is the same for other temperatures. ^bRefers to the calculated hyperfine field per Fe–Se–Fe superexchange interaction based on A and B sites. ^cRefers to the calculated hyperfine field per Fe–Se–Fe superexchange interaction based on B and C sites.

We therefore expect that all Fe ions are equally reduced from Fe^{3+} . This can be caused by the well-known fast electron exchange between octahedrally coordinated Fe^{2+} and Fe^{3+} , which gives an intermediate valence state. The same phenomenon is also observed in Fe_3S_4 and Fe_3O_4 , in which metallic conductivity is reported when fast exchange occurs.³¹

The three sextets are characterized at 80 K by three distinct hyperfine fields of 274.3(3), 226.6(6), and 202.0(4) kOe for the A, B, and C sites, respectively. They can be attributed to three magnetically nonequivalent Fe sites in the superstructure, as illustrated in Figure 1. The A sites (atom to the right of the letter “A”) are in an ab plane with Fe vacancies, where two adjacent ferromagnetic cation sites are vacant. The B and C sites are in planes with no Fe vacancies but with different numbers of adjacent antiferromagnetic cations (four for the B site and three for the C site). This can be inferred from the complicated exchange interactions in the 3c- Fe_7Se_8 superstructure. Briefly, there are four inter- and intralayer exchange interactions, as illustrated in Figure 9b. The Fe–Fe

Figure 10. (a) Measurement and fit of the temperature dependence of the resistivity with the Mott VRH model. (b) Illustration describing electron localization across domain boundaries. (c) XPS spectrum of the 3c sample. (d) Temperature dependence of the resistivity of 4c- Fe_7Se_8 . The arrows indicate the gradual spin rotations between 100 and 240 K.

ferromagnetic interaction J_1 should be relatively small due to the large Fe–Fe distance (~ 3.6 Å). The Fe–Se–Fe superexchange interaction J_2 involves three Se ions below and above the Fe layer, where the angle of the Fe–Se–Fe bond is 96.3° and the Fe–Se distance is 2.6 Å. The interlayer Fe–Se–Fe superexchange interactions can be divided into two non-equivalent bonds, although they have similar Fe–Se bond distances (2.6–2.7 Å). Only the Fe–Se–Fe bonds with an angle of $\sim 127.6^\circ$ are effective for an antiferromagnetic interaction ($J_3 < 0$). The bonds with an angle of $\sim 70^\circ$ (J_4) give no effective d–p interaction. This is same as the 3c- Fe_7Se_8 superstructure. Thus, the intralayer interactions and some of the Fe–Se–Fe superexchange interactions are weaker than the 127.6° Fe–Se–Fe superexchange interactions, i.e., $J_3 \gg J_4 > J_2 > J_1$. In this case, the A, B, and C sites have 18, 14, and 13 interlayer superexchange links, respectively. This is in good agreement with our measurement of the hyperfine fields and is confirmed by other groups,^{42,43} as displayed in Table 1.

However, two interesting phenomena should be noted here. First, the hyperfine field at the A site increases from 274.3 kOe at 80 K to 278.12 kOe at 110 K. On the other hand, the values at the B and C sites decrease with increasing temperature, as expected because of the increased thermal energy. The second phenomenon is the change of the hyperfine field ratio between the B and C sites as a function of the temperature. Basically, the hyperfine field H_{hf} at Fe nuclei can be expressed as a vectorial sum of four main contributions:⁴⁴

$$\vec{H}_{\text{hf}} = \vec{H}_{\text{d}} + \vec{H}_{\text{orb}} + \vec{H}_{\text{cp}} + \vec{H}_{\text{STHF}} \quad (6)$$

where H_{d} is the dipolar term on the order of 2 T and H_{orb} is the orbital field, which can be neglected due to the quenching of the orbital momentum by the crystal field. H_{cp} represents the field due to polarization of the core electrons (1s, 2s, and 3s); this term is proportional to the 3d shell magnetic moment

according to the theoretical calculations by Watson and Freeman.⁴⁵ The term H_{STHF} is the supertransferred hyperfine field (STHF), which is a result of the transfer of the spin density from cations with spin-up ($\uparrow$) to the neighboring cation with spin-down ($\downarrow$) via superexchange. H_{cp} and H_{STHF} have the same direction and increase the total field H_{hf} while H_{orb} is positive and reduces the field at Fe nuclei. With this in mind, we can conclude that the increase of the hyperfine field on the A site is the result of the reorientation of the spins around 100 K. This is consistent with the ZFC–FC curves, as well the temperature-dependent saturation magnetization, where an increase of the magnetization is observed at the same temperature. The values of H_{STHF} for the three nonequivalent sites are quite different depending on the nearest Fe neighbors. The appearance of vacancies results in fewer Fe–Se–Fe superexchange links and reduces the corresponding fields. This is also the reason why we attribute the largest hyperfine field to the Fe ions located in the vacancy layer (A site). The average value of the H_{STHF} term can be estimated as ~ 15 kOe per Fe–Se–Fe superexchange link. We calculate the decreased fields based on the different numbers of Fe–Se–Fe superexchange links at the B and C sites, and the results are listed in Table 1. An excellent agreement is observed in all temperatures. The values are 10–20 kOe per Fe–O–Fe superexchange link in oxides at 4.2 K⁴⁶ and 10 kOe per Fe–S–Fe superexchange link in sulfides at 80 K.³¹ The increasing value per interaction is the result of the stronger covalent bonding between the cations and ligands in chalcogen-based compounds. Apparently, with increasing temperature, both the B and C sites lose some Fe–Se–Fe superexchange interactions (much more so in the case of C sites) in the experimental temperature regime. This may be caused by an increase or redistribution of vacancies in the adjacent antiferromagnetic Fe layers. Such a redistribution will break the ordering of Fe vacancies, and the electronic states responsible for charge transport are localized near these

disordered vacancy areas.¹ Such Anderson localization explains well the appearance of Mott variable range hopping (VRH) conductivity in the investigated samples, as shown in the following section. Further evidence is provided by the decreasing 4s electron density, as indicated by the increasing isomer shift from 0.8253 mm/s at 80 K to 0.8350 mm/s at 110 K at the C site. The same phenomenon was observed in ultrathin epitaxial Fe films covered with different overlayers.⁴⁷ Localization happens at the interface between the Fe film surface and the overlayer material.

3.5. Metal–Insulator Transition Mechanism. The abrupt change in the direction of the magnetic moment at 100 K, in combination with the existence of rich boundaries in the synthesized samples, yields an alternative interpretation for the metal–insulator transition at 100 K. We propose that it is caused by electron localization in the defect areas responsible for this transition. We can model the temperature-dependent resistivity above 100 K by a VRH mechanism:

$$\rho(T) = \rho_0 \exp \left[\left(-\frac{T_{\text{Mott}}}{T} \right)^{1/4} \right] \quad (7)$$

where ρ_0 is a prefactor, T_{Mott} is the characteristic hopping temperature, $\gamma = 1/4$ is the hopping power, which depends on both the dimensionality of the system and the shape of the DOS at the Fermi level. As shown in Figure 10a, an excellent fit can be obtained with the power $1/4$, typical for three-dimensional Mott VRH conduction with noninteracting charge carriers. The Mott VRH describes transport from 250 to 100 K and deviates only at lower temperatures. The observation of VRH of localized states induced by disorder suggests that localization mechanisms play a role in this temperature regime. In fact, Mott VRH is not only observed for insulators or semiconductors but also for metals and superconductors. Here, a MI transition occurs with small changes in the crystal structure. The grain boundaries, as well as all intrinsic defects, have the ability to markedly alter electronic transport in Fe₇Se₈.⁴⁸ The same phenomenon has been reported for two-dimensional structures separated by grain boundaries. A significant degradation in the electrical and mechanical properties is observed. The contributions from the intergrain resistivity can be up to 10 times higher than those from the intragrain resistivity.⁴⁹ In addition, considering the large number of vacancies, localized states superimposed on a structureless finite DOS can be induced around the vacancies. The source of electron localization may originate from the spin rotation in the present system. Above 100 K, some of the moments in the boundary areas are locked and act as pinning centers. This can produce a noncollinear magnetic structure in the interfacial areas, as illustrated in Figure 10b. It is expected that in such a noncollinear system the electronic wave functions will adopt an extended or localized nature depending on the direction of the plane in which the spins rotate.⁵⁰ Consequently, a large difference in the resistivity may result between parallel and perpendicular spins with respect to the rotation axis. This also explains why three-dimensional Mott VRH dominates electrical transport. In the present samples with randomly distributed grain boundaries, the charge carriers cannot pass from localized states to the nearest-neighbor unoccupied sites but hop in three dimensions between any possible empty sites that have a smaller energy difference.

Evidence for electron localization can be obtained from the Fe 2p XPS spectrum, as shown in Figure 10c. The

contributions at binding energies of 710.8 and 711.8 eV can be attributed to the Fe 2p_{3/2} orbitals of Fe²⁺ and Fe³⁺, respectively.^{51,52} This is consistent with our expectation that Fe₇Se₈ should have both Fe²⁺ and Fe³⁺ for electron neutrality. We also observe the corresponding satellite peaks at binding energies of 715.6 and 719.5 eV. These can be used for determination of the oxidation state and chemical environment.⁵³ Generally, in the Fe 2p, the photoemission line of Fe³⁺ is broader compared to that of Fe²⁺ and the satellite peak for Fe³⁺ is observed at ~8.0 eV higher binding energy than the Fe 2p_{3/2} main peak. For Fe²⁺, the satellite peak is located about 5.0 eV above the main peak. Compounds with mixed-Fe valence such as Fe₃O₄ have no satellite peaks.⁵³ Therefore, the two observed peaks at higher binding energy can be ascribed to charge-transfer satellites of Fe²⁺ and Fe³⁺. In the X-ray photoemission process, the suddenly created core hole will strongly interact with the valence electrons. This effect is relatively small in weakly correlated materials, where the dominant excitations are plasmons,⁵⁴ but quite significant in strongly correlated systems such as 3d transition-metal compounds. The strong core-hole potential, resulting from the large CI strength between the core hole and 3d electrons, reflects the localized nature of the 3d states and favors the transfer of electrons to the 3d states in order to screen out the core-hole charge.⁵⁵ This corresponds to the shakeup excitations in XPS characterized by a satellite peak at higher binding energy, especially at the materials surface, where many defects exist. The strong charge-transfer satellites observed in our samples therefore point to electron localization at grain boundaries or at the sample surface, where it is easy to form defects.

As further evidence, the electrical transport properties of 4c-Fe₇Se₈ were also investigated and are displayed in Figure 10d. As we discussed in the Introduction, the directions of the magnetic moments in the 4c structure rotate gradually above 100 K and the rotation is complete at around 240 K. In accordance with our model, this sample shows a much better conductivity because of the high-temperature sintering. Interestingly, the resistivity changes slope at 100 K, and a metal–insulator transition is observed when the spin rotation is complete at around 240 K.

4. CONCLUSION

We have synthesized high-quality samples of the 3c-Fe₇Se₈ superstructure. Resistivity measurements show a metal–insulator transition near 100 K, at the same temperature as that of a spin rotation. This contradicts our theoretical calculations that 3c-Fe₇Se₈ should be a metal, regardless of the vacancy concentration and distribution. Magnetic measurements confirm the existence of extra pinning centers below the transition, characterized by the divergence between the ZFC and FC curves. Considering the existence of grain boundaries observed by HRTEM, we propose that electron localization is caused by the formation of a noncollinear magnetic structure in the interfacial areas. This spin-rotation-induced localization is confirmed by XPS measurements and a comparison with the properties of the 4c-Fe₇Se₈ superstructure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02257.

DFT calculations, SEM image of pure Fe₇Se₈ with a 3c structure, magnified SEM image showing the existence of numerous nanoparticles (Figure S1), DOS for these seven cases with Fe defects in a hexagonal 3c structure (Figure S2), and optimized lattice parameters and calculated total magnetization of Fe₂₁Se₂₄ with different values of *U* considered in the DFT calculations (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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