Canted Antiferromagnetism in the Quasi-1D Iron Chalcogenide BaFe$_2$Se$_4$

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We report the synthesis and physical properties studies of quasi-1D iron chalcogenide BaFe$_2$Se$_4$ which shares the FeSe$_4$ tetrahedra building motif commonly seen in the iron chalcogenide superconductors. A high-quality polycrystalline sample was achieved by solid-state reaction method and characterized by X-ray diffraction, electrical resistivity, magnetic susceptibility and neutron diffraction measurements. BaFe$_2$Se$_4$ is a narrow gap semiconductor that magnetically orders at $\sim 310$ K. Both neutron powder diffraction results and isothermal $M$-$H$ loops suggest a canted antiferromagnetic structure where Fe sublattice are antiferromagnetically ordered along the $c$-axis quasi-1D chain direction, resulting in a net ferromagnetic moment in the perpendicular direction along the a-axis with tilted angle of $18.7^\circ$ towards the b-axis.

The discovery of iron-based superconductors$^{12}$ has significantly changed the landscape of unconventional superconductivity in the past decade. Among all the iron-based superconductors, two major chalcogenide-based families have been intensively studied. First, the FeSe, with the simplest crystal structure and bulk superconductivity at 8 K at ambient pressure$^{12}$ and at 37 K under high pressure$^{10,12}$, has caught particular research interest in the past few years due to the significantly enhanced interfacial superconductivity with $T_c$ up to 65 K found in the epitaxial single-layer FeSe/SrTiO$_3$ system$^{10-15}$. The second major family is alkali metal (A = K, Rb, Cs, and Tl) intercalated $A_1-x$Fe$_2$Se$_2$ superconductors with $T_c \sim 30$ K$^{16,22}$ where the interplay of vacancy order, magnetism, orbital-selective Mott phase, and superconductivity have been intensively studied$^{22-26}$. New chemical intercalation routes also result in several new superconductors with higher $T_c$ such as the Li$_4$(NH$_3$)$_2$Li$_3$Fe$_2$Se$_2$ ($x \sim 0.6$; $y \sim 0.2$), and (Li,Fe)OHFeSe. Nevertheless, the essential charge carrier layers of these chalcogenide superconductors, two-dimensional (2D) Fe$_2$Se$_2$ square lattice formed by the edge-sharing FeSe$_4$ tetrahedra, are the fundamental building block of all the Fe-based superconductors.

The spin-ladder compound BaFe$_2$Se$_4$ is structurally related to the iron chalcogenide superconductors mentioned above, but with a reduced dimensionality. The structure consists of the same building motif, edge-sharing FeSe$_4$ tetrahedra, but stacked along the $b$-axis thus forming unique quasi-one-dimensional (quasi-1D) double chains of Fe$_2$Se$_3$ instead of the 2D Fe$_2$Se$_2$ lattice seen in the iron chalcogenide superconductors. It exhibits unique spin-ladder magnetic structure and long-range-ordered antiferromagnetic order below $T_N \sim 250$ K, and short-range magnetic correlations at room temperature$^{34,35}$. The antiferromagnetic changes from block-type in BaFe$_2$Se$_4$ to stripe-type in BaFe$_2$S$_3$, KFe$_2$Se$_3$, and CsFe$_2$Se$_3$.$^{36,37}$ Interestingly, superconductivity has been reported in both BaFe$_2$Se$_3$ and BaFe$_2$S$_3$ compounds under high pressure, with $T_c \sim 11$ K$^{38}$ above 10 GPa for BaFe$_2$Se$_3$, and $T_c \sim 24$ K above 10 GPa for BaFe$_2$S$_3$$^{39}$, respectively. They are the only reported materials so far to exhibit a superconducting phase under pressure in this spin-ladder family. This is rather intriguing as the superconductivity in BaFe$_2$Se$_3$ emerges near a possible orbital-selective Mott-insulator$^{22}$, which might provide additional insight into the understanding of the 2D iron chalcogenide superconductors.

BaFe$_2$Se$_4$ is another new quasi-1D iron chalcogenide based on the FeSe$_4$ tetrahedra building motif but with a simpler and different structure from that of the BaFe$_2$Se$_3$ compound. The difference between the two crystal structures of BaFe$_2$Se$_4$ and BaFe$_2$S$_3$ is shown in Figure 1. Unlike the spin-ladder double chains in the BaFe$_2$Se$_3$, the quasi-1D chain in the BaFe$_2$Se$_4$ consists only of single chains of edge-sharing FeSe$_4$ tetrahedra along the $c$-axis separated by Ba atoms. Figure 1b and Figure 1c are highlighting the quasi-1D chain along different directions. The interlayer chains are well separated from each other, with a Fe-Fe distance between the interlayer neighboring 1D Fe chains of 5.663(1) Å and the closest Se-Se distance of 3.489(8) Å. On the other hand, within the quasi-1D chain (Figure 1a), the Fe-Fe interchain distance is 2.742(9) Å and the Fe-Se distance within the FeSe$_4$ tetrahedra is 2.349(5) Å. Both are pretty comparable with the distances in the BaFe$_2$Se$_3$ and other iron chalcogenide superconductors.

However, to date, only the structural determination based on small grains ($\sim 50$ μm) has been reported for this compound$^{40}$. Previous synthesis attempts from pure elements and repeated regrinding/annealing using different temperature profiles up to 1100 °C do not yield an X-ray powder pure phase$^{40}$. Therefore, no systematic transport and magnetic characterizations have been carried out on this compound. Band structure calculations, on the other hand, suggest the Fermi level of this com-
one-third of the trace of the orthogonalized $U_{eq}$ tensor.

| Atom | Wyck. | $x$  | $y$  | $z$  | $U_{eq}(\text{Å}^2)$  |
|------|-------|------|------|------|----------------------|
| Ba   | 2b    | 1/2  | 1/2  | 0    | 0.0411(6)            |
| Se   | 8h    | 0.70360(6) | 0.12350(6) | 0    | 0.0195(3)            |
| Fe   | 4d    | 1/2  | 0    | 1/4  | 0.0167(6)            |

FIG. 1: (a) Schematic crystal structure of BaFe$_2$Se$_4$ and BaFe$_2$Se$_3$. Both compounds adopt similar quasi-1D structure consist of edge-sharing FeSe$_4$ tetrahedra, forming single chains in BaFe$_2$Se$_4$ while double chains in BaFe$_2$Se$_3$. (b) the view from the $b$-axis for BaFe$_2$Se$_4$ (c) The detailed microstructure of infinite chains of edge-sharing FeSe$_4$ tetrahedra along the $c$-axis for BaFe$_2$Se$_4$. (d) X-ray diffraction pattern and Rietveld refinement results of the BaFe$_2$Se$_4$ at room temperature. The black circles are experimental data, the red curve is the Rietveld refinement fit, and the green curve is the difference. The tick marks indicate the allowed Bragg reflections.

TABLE I: Refined atomic position at room temperature from Rietveld analysis for BaFe$_2$Se$_4$ in the $I4/m$ space group with $a = 8.0150(1)$ Å, and $c = 5.4936(2)$ Å. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{eq}$ tensor.

Contrast to the previous calculation results, we show that the compound is actually semiconducting with an excitation energy of $\sim 142$ meV. More importantly, it contains a unique magnetic transition at $\sim 310$ K caused by canting antiferromagnetic interactions between the neighboring Fe-Fe atoms based on magnetic susceptibility and neutron diffraction studies.

The BaFe$_2$Se$_4$ polycrystalline sample was synthesized by the solid-state reaction method using elemental Ba pieces (Alfa Aesar, 99+%), Fe granules (Alfa Aesar, 99.98%) and Se shots (Alfa Aesar, 99.999%). The reaction was carried out at 700 °C in the sealed quartz tube for 2 days, followed by slowly cooling down to room temperature in 10 hours. In particular, two strategies have been utilized during the synthesis to ensure the high-quality powder synthesis and to avoid the formation of small yet magnetic FeSe$_2$, Fe$_7$Se$_8$, Fe$_{1-x}$Se and other Fe related impurities phases as commonly seen in the previous reports and other ternary iron chalcogenide phases: (1) an excess of $\sim 5\%$ Se was used to compensate the Se lost during the initial reaction from elements. (2) after the initial reaction, small representative sample is scanned by X-ray diffraction (XRD) for initial screening of phase purity where a small amount of FeSe ($< 5\%$ based on XRD analysis) is detected. To further remove this impurity and potentially other amorphous impurities that could not been detected by XRD, a precise amount of BaSe$_3$ corresponding to that needed to facilitate the reaction of BaSe$_3$ + FeSe $\rightarrow$ BaFe$_2$Se$_4$ is added to the bulk powder, and is reground together with the samples. The assembly is pelletized and annealed at slightly lower temperature 600 °C for 2 weeks. To further improve homogeneity and quality of the samples, several cycles (> 2 times) of regrinding and longtime annealing (> 2 weeks) at 600 °C are also carried out. A typical run of the sample normally takes more than 6 weeks to be finished. Such prolonged annealing time also exclude the formation of amorphous impurities as well. The obtained BaFe$_2$Se$_4$ sample is stable in air, and we do not observe any impurity peaks based on XRD analysis and magnetic susceptibilities measurement.

The powder sample was characterized at room temperature by XRD using a Rigaku Smartlab diffractometer and the Rietveld refinements were carried out using FULLPROF and GSAS software packages. The XRD pattern of the synthesized BaFe$_2$Se$_4$ sample and corresponding structural refinement results are presented in Figure 1 and Table I. Based on the Rietveld analysis, the synthesized BaFe$_2$Se$_4$ sample crystallizes in the tetragonal space group $I4/m$ (87) with $a = b = 8.0150(1)$ Å, and $c = 5.4936(2) \text{ Å}$, consistent with the values reported in early literature. All diffraction peaks for BaFe$_2$Se$_4$ can be well indexed and no impurities are detected within XRD resolution. Together with the good refinement values $R = 1.71\%$ and $R_{wp} = 2.52\%$, this suggests high quality of our synthesized BaFe$_2$Se$_4$ powder sample.

The electrical transport was measured with Quantum
Design PPMS, using the standard four-probe method. The temperature dependent electrical resistivity data are shown in Figure 2. The resistivity shows an overall semiconducting behavior, which is in contradiction with previous band structure calculations, but in agreement with the measurement reported for its isostructural counterpart BaFe$_2$Se$_4$. We note that the resistivity value at room temperature is 35.5 Ω cm, which is slightly larger than that of spin-ladder compound BaFe$_2$Se$_3$ (17 Ω cm$^{[12]}$). The resistivity can be fit quite well using thermal activation model $\rho = \rho_0 \exp(\Delta/k_B T)$, where $\rho_0$ is a prefactor, and $k_B$ is the Boltzmann constant. The inset of Figure 2 shows the results of linear fitting of $\ln(\rho)$ vs. $1/T$, which is consistent with the standard activation model. The activation energy estimated from the fitting is $\Delta = 142.5$ meV, which is comparable to the reported gap value of BaFe$_2$Se$_3$ ($\sim$ 180 meV$^{[5]}$).

![Figure 2: Temperature dependence of resistivity on BaFe$_2$Se$_4$ and the inset shows fitting results from $\ln(\rho)$ vs. $1/T$.](image)

The dc magnetic susceptibility and field-dependent magnetization were measured with Quantum Design MPMS down to 5 K and up to 5 T. The temperature dependence of the magnetization of BaFe$_2$Se$_4$ from 5 K to 350 K under different magnetic fields is presented in Figure 3. A spontaneous magnetization appears at $\sim$ 310 K and increases monotonically below this transition with decreasing temperature. Together with the clear splitting of magnetization between the zero-field-cooled (ZFC) and field-cooled (FC) mode, this indicates the existence of a ferromagnetic component below the transition temperature. The $M_{ZFC}$ and $M_{FC}$ splitting becomes weaker with an increasing magnetic field eventually nearly overlapping at 1 T. The magnetization starts to saturate to a nearly constant plateau below about 50 K. Increasing the applied magnetic field increases the absolute value of the magnetization, but the change of transition temperature $T_c$ is rather small ($< 5$ K). The exact transition temperature is tracked best in the temperature derivative of the normalized magnetization $dM/HdT$, depicted in inset of Figure 3. No traceable magnetic transition at $\sim$ 120 K from Fe-Se binary phase (Fe$_4$Se$_x$) is observed, further suggesting the success of our synthetic approach for high-quality samples. A small blip at $\sim$ 50 K in ZFC data at 1 T was observed which is due to some trapped oxygen in the powder samples, which is non-intrinsic signal of BaFe$_2$Se$_4$ sample. To obtain the effective magnetic moment of Fe in BaFe$_2$Se$_4$, we performed Curie-Weiss fitting over the high-temperature range. To eliminate the influence of ferromagnetic behavior, the temperature range between 330 K and 350 K was chosen at where the $M(T)/H$ curves of 100 Oe, 1000 Oe, and 1 T overlap with each other. The susceptibility does follow the Curie-Weiss law $\chi = C/(T - \theta)$ quite nicely, with Curie constant $C = 2.82$ emu K/mol and Curie temperature $\theta = 329$ K. The resulting Curie constant corresponds to an effective magnetic moment of $\mu_{\text{eff}} = 3.36 \mu_B$/Fe (4.75 $\mu_B$/f.u.). The positive $\theta$, which is close to the transition temperature, on the other hand, indicates ferromagnetic interactions in the samples.

The field dependence measurements of the magnetization for BaFe$_2$Se$_4$ from -5 T to 5 T at different temperatures from 20 K to 350 K were carried out to further explore the nature of magnetic orders and are shown in Figure 4. A weak yet clear magnetic hysteresis has been observed below 310 K, however the magnetization did not saturate at a high magnetic field, instead, linear dependent $M$-$H$ curves suggest an antiferromagnetic state is observed. The magnetic hysteresis loop is suppressed with increasing temperature and eventually disappears and becomes a straight line by 350 K. No hysteresis nor clear remnant signal is observed in the isothermal $M$-$H$ loop at 350 K, suggesting the ferromagnetic components are not due to amorphous iron or iron oxide impurities, which all have a Curie temperature above 450 K. This further suggests that the observed concurrence of the ferromagnetic and antiferromagnetic state is an intrinsic property of our samples. For a high-quality pure phase, this $M$-$H$ behavior is consistent with the canted antiferromagnetic state in the BaFe$_2$Se$_4$ system in which the ferromagnetic order is provided by the small component canted by magnetic moment of Fe.

The hysteresis loop at 20 K closes up at the field value $H \sim 2.6$ T and shows a coercive field of $H_c = 5.6$ kOe. The linear antiferromagnetic behavior appears hold up to 5 T, the highest field we have measured. To extract the saturation moment caused by the ferromagnetic component, the $M(H)$ curve at the high field was fit using $M(H) = M_S + M_{AFM}$, where $M_S$ is the saturation moment which is field independent at the high magnetic field and $M_{AFM}$ is the antiferromagnetic contribution which has a linear relationship to the magnetic field. Through this fitting, we are able to subtract the linear contribution $\chi_{AFM}H$ from the experimental data, as shown in the inset of Figure 4. The moment of the ferromagnetic component could also be extracted from the saturated magnetization, from which we obtained $\sim 0.013 \mu_B$/Fe. This value is way smaller than the effective moment calculated by Curie-Weiss law, which further supports the
The temperature dependent NPD data, as seen in Figure 4a, show a diffraction pattern taken at 280 K along with Rietveld refinement results obtained using FULLPROF. All Bragg peaks can be fit with the Rietveld refinement. The obtained refinement values $\chi^2 = 6.10$, $R_{wp} = 13.1$, and the $R$ Bragg factor for the refinement of nuclear and magnetic phases are 4.278 and 17.55, respectively. There are three additional Bragg peaks at $Q \sim 2.7$, 3.1, and 4.4 Å$^{-1}$, which belong to the aluminum sample holder and were added to the structural refinement as the minor phase. As the temperature is further decreased to 2 K, there is an increased intensity, centered at $Q \sim 1.4$ Å$^{-1}$, that is not described by the nuclear phase and likely originated from the magnetic phase.

To identify the magnetic structure, we further performed a full representational analysis for NPD data at 2 K to determine possible irreducible representations (irreps) and basis vectors (BVs) to describe the magnetic structure using the SARAh code. There is a total of 6 possible basis vectors corresponding to 6 irreps $\Gamma_1$, $\Gamma_3$, $\Gamma_4$, $\Gamma_6$, $\Gamma_7$, $\Gamma_8$. They are labeled following the scheme of SARAh and Kovalev in Table SI in the Supplemental Material. Each irrep describes the magnetically distinct atoms within the unit cell. Within each irrep, each BV describes the possible direction of magnetic moments pointing along the $a$, $b$, and $c$-axis. We discriminated between all BVS by comparing the refinement values $\chi^2$ and $R$ factors and found that both $\Psi_3$ and $\Psi_5$ are required in order to obtain the best fit, as shown in Figure 3b. The $\Psi_3$ and $\Psi_5$ are from two different irreps implies that either there are two transitions or a strong first order transition. From the $M$-$T$ plots presented in Figure 3a, only one transition was observed, therefore a first order transition seems more likely to be presented in BaFe$_2$Se$_4$. The $\Psi_5$ indicates a ferromagnetic moment along the $b$-axis, while $\Psi_5$ suggests an antiferromagnetic moment along the $a$-axis, which further confirms the canted antiferromagnetic spin alignment in BaFe$_2$Se$_4$. The obtained refinement values $\chi^2 = 6.82$ and $R_{wp} = 12.6$. The $R$ Bragg factors for the refinement of nuclear and magnetic phases are 4.898 and 5.758, respectively.

The obtained magnetic structure of BaFe$_2$Se$_4$ can be described as Fe spins aligned perpendicular to the 1D molecular chains, antiferromagnetically correlated along the chain direction (the $c$-axis) as well as the interchain direction (the $a$-axis), with spins along the $a$-axis, and a small ferromagnetic canting along the $b$-axis, as shown in the inset of Figure 3a. The magnitude of the magnetic moment estimated from NPD data is 2.09 $\mu_B$/Fe, with 1.98 $\mu_B$/Fe along the $a$-axis and 0.67 $\mu_B$/Fe along the $b$-axis. The magnetic moment canting angle is $\sim 18.7^\circ$ from the $a$-axis. Because of thermal fluctuations, a larger tilted angle of 63.1$^\circ$ is observed at 280 K comparing to 18.7$^\circ$ at 2 K. For comparison, in the tetrahedrally coordinated system, due to the crystal field effect, the magnetic moment of a free Fe$^{3+}$ ion is 5.92 $\mu_B$ for the high spin

![](image_url)
state and 1.73 \( \mu_B \) for the low spin state taking the Lande factor \( g = 2 \). The calculated magnetic moment is in between the high spin and low spin state indicating a possible mixed state in this system. The magnitude of the magnetic moment is pretty close to that of single-chain quasi-1D TiFeSe_2 material with the same formal Fe\(^{3+}\) valence, but smaller than that of spin-ladder quasi-1D iron chalcogenide BaFe_2Se_3 with a formal Fe\(^{2+}\) valence. In TiFeSe_2, the FeSe_4 tetrahedra also form a quasi-1D structure with Néel temperature at 295 K and the magnetic moment of Fe is 2.1 \( \mu_B/Fe \). The similar single 1D chain in both BaFe_2Se_3 and TiFeSe_2, leads one to expect that both materials have similar direct and indirect exchange interactions. However, the Dzyaloshinskii-Moriya interaction also arises, and this anisotropic exchange interaction leads to the canted antiferromagnetic ground state in the BaFe_2Se_3. On the other hand, this canted antiferromagnetic structure in BaFe_2Se_3 is quite different from the typical magnetic structures discovered in spin-ladder quasi-1D iron chalcogenides, such as block-type structure in BaFe_2Se_3, where four Fe spins along the chain form a Fe_4 ferromagnetic block, and each Fe_4 block stacks antiferromagnetically, or stripe-type structure in BaFeS_3, KFe_2Se_3 and CsFe_2Se_3, where Fe spins are ferromagnetic coupled along the rung direction and each ferromagnetic unit stacks antiferromagnetically along the leg direction.

The observation of the canted antiferromagnetism in this quasi-1D BaFe_2Se_4 compound is rather intriguing and could be a playground to further explore the correlations between magnetism and superconductivity. The antiferromagnetic order and/or magnetic spin fluctuations have been universally observed in the iron-based superconductors, and plays an important role for the emergence of superconductivity in BaFe_2Se_4, with a simpler structure and higher symmetry than spin-ladder phase BaFe_2Se_3, will provide a unique opportunity to reveal the intimate interplay between magnetism, crystal lattice and electronic structure in [FeX_3]-based materials, and perhaps to understand the mechanism of superconductivity in Fe-based compounds. The BaFe_2Se_3 becomes superconducting at \( \sim 11 \) K at high pressure \( > 10 \) GPa. The appearance of superconductivity in BaFe_2Se_3 has a strong correlation with the magnitude of magnetic moments of Fe atoms, and the magnitude of magnetic moments is gradually decreasing with increasing pressure. It will be interesting to investigate how the magnetic structure and moment, canted antiferromagnetic correlation, and ferromagnetic component evolve with chemical doping or high pressure, whether superconductivity could be induced in the vicinity of this canted antiferromagnetism and how it interplays with the antiferromagnetism or even ferromagnetism when it emerges.

In summary, we have successfully synthesized high-quality polycrystalline sample of quasi-1D iron chalcogenide BaFe_2Se_4. It has a semiconducting behavior with activation energy \( \sim 142 \) meV. Magnetic susceptibility measurements suggest a ferromagnetic-like transition at \( \sim 310 \) K, and NPD further reveals it is actually canted antiferromagnetism correlated along the 1D chain direction with a net small ferromagnetic moment in the perpendicular direction. The magnitude of the magnetic moment estimated from NPD data is 2.09 \( \mu_B/Fe \), which is pretty close to that of quasi-1D TiFeSe_2 material with the same Fe\(^{3+}\) valence, but smaller than that of other quasi-1D iron chalcogenides such as BaFe_2Se_3 with Fe\(^{2+}\) valence. This canted antiferromagnetic structure is also different from the typical block-type or stripe-type magnetism discovered in the quasi-1D iron chalcogenide such as BaFe_2Se_3 and BaFe_2S_3, and could provide unique playground to study the interplay between magnetism,
crystal lattice and electronic structure in the Fe-based compounds.

This work at University of Texas at Dallas is supported by US Air Force Office of Scientific Research (FA9550-19-1-0037), and National Science Foundation (DMR 1921581). We also acknowledge the support from the Office of Research at University of Texas at Dallas through the Seed Program for Interdisciplinary Research (SPIRe) and the Core Facility Voucher Program. Support from Advanced Materials and Manufacturing Processes Institute (AMMPI) at the University of North Texas is acknowledged.

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**Supplemental Material for ‘Canted Antiferromagnetism in the Quasi-1D Iron Chalcogenide BaFe$_2$Se$_4$’**

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Table SI: Basis vectors (BV) of irreducible representations (irreps) for the space group $I_4/m$ with the magnetic propagation vector $k = (0, 0, 0)$

| Irreps | BVs | Atoms     | $m_a$ | $m_b$ | $m_c$ |
|--------|-----|-----------|-------|-------|-------|
| $\Gamma_1$ | $\Psi_1$ | Fe1 0 0 4 | 0     | 0     | 4     |
|         |       | Fe2 0 0 4 | 0     | 0     | 4     |
| $\Gamma_3$ | $\Psi_2$ | Fe1 4 0 0 | 4     | 0     | 0     |
|         |       | Fe2 4 0 0 | 4     | 0     | 0     |
| $\Gamma_4$ | $\Psi_3$ | Fe1 4 0 0 | 4     | 0     | 0     |
|         |       | Fe2 −4 0 0 | 0     | 0     | 0     |
| $\Gamma_6$ | $\Psi_4$ | Fe1 0 0 4 | 0     | 0     | 4     |
|         |       | Fe2 0 0 −4 | 0     | −4    | 0     |
| $\Gamma_7$ | $\Psi_5$ | Fe1 0 −4 0 | 0     | −4    | 0     |
|         |       | Fe2 0 −4 0 | 0     | −4    | 0     |
| $\Gamma_8$ | $\Psi_6$ | Fe1 0 4 0 | 0     | 4     | 0     |
|         |       | Fe2 0 −4 0 | 0     | −4    | 0     |