Antiferromagnetism in semiconducting KFe$_{0.85}$Ag$_{1.15}$Te$_2$ single crystals

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(Received 3 May 2011; published 16 August 2011)

We have synthesized single crystals of K$_{1+2x}$Fe$_{0.85y}$Ag$_{1.15z}$Te$_2$ by introducing alkali metal atomic layers between FeCh sheets. Further studies indicate that in the new superconductors the $T_c$ gets enhanced when compared to FeCh-11 materials, but there is also a set of distinctive physical properties. FeCh-122 materials are close to the metal-semiconducting crossover and antiferromagnetic (AFM) order. This is in contrast to other superconductors which are in close proximity to the spin-density wave state. The Fermi surface in FeCh-122-type Fe-HTSs contains only electronlike sheets without the nesting features found in most other Fe-HTS.

On the other hand, superconductivity in FeCh-11 materials is quite robust with respect to anion change, as seen on the example of FeSe$_{1-x}$, FeTe$_{1-x}$, and FeTe$_{1-x}$S$_x$. However, in FeCh-122 compounds, superconductivity is only observed in A$_x$Fe$_{2-y}$Se$_2$ or K$_x$Fe$_{2-y}$Se$_2$-S$_y$, while pure K$_x$Fe$_{2-y}$S$_2$ is a semiconductor with spin-glass transition at low temperature. Moreover, the theoretical calculation indicates that the hypothetical KFe$_2$Te$_2$, if synthesized, would have higher $T_c$ than K$_x$Fe$_{2-y}$Se$_2$. Therefore, synthesis and examination of physical properties of FeCh-122 materials containing FeTe layers could be very instructive.

In this Rapid Communication we report discovery of K$_{1.00(3)}$Fe$_{0.85(2)}$Ag$_{1.15(2)}$Te$_2$0.1 single crystals. The resistivity and magnetic measurements indicate that this compound has the semiconducting long-range AFM order at low temperature, with no superconductivity down to 1.9 K.

Single crystals of KFe$_2$Ag$_2$Te$_2$ were grown by the self-flux method reported elsewhere in detail, with nominal composition K:Fe:Ag:Te = 1:1:1:2. Single crystals with typical size 5×5×2 mm$^3$ can be grown. Powder x-ray diffraction (XRD) data were collected at 300 K using 0.3184 Å wavelength radiation (38.94 keV) at the X7B beamline of the National Synchrotron Light Source. The average stoichiometry was determined by examination of multiple points using an energy-dispersive x-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope. Electrical transport measurements were performed using a four-probe configuration on rectangular-shaped polished single crystals with current flowing in the $ab$ plane of tetragonal structure. Thin Pt wires were attached to electrical contacts made of silver paste. Electrical transport, heat capacity, and magnetization measurements were carried out in Quantum Design PPMS-9 and MPMS-XL5.

Figure 1(a) shows powder XRD results and structural refinements of K(Fe,Ag)$_2$Te$_2$ using a general structure analysis system (GSAS). It can be seen that all reflections can be indexed in the $I4/mmm$ space group. The refined structure parameters are listed in Table I. The determined lattice parameters are $a = 4.3707(9)$ Å and $c = 14.9540(8)$ Å, which are reasonably smaller than those of CsFe$_2$Ag$_{2-y}$Te$_2$ [$a = 4.5058(4)$ Å and $c = 15.4587(8)$ Å$]^{14}$, but much larger than those of K$_x$Fe$_{2-y}$Se$_2$ and K$_x$Fe$_{2-y}$S$_2$. Due to the smaller ionic size of K$^+$ than Cs$^+$ and larger size of Ag$^+$ and Te$^{2-}$ than Fe$^{2+}$ and Se$^{2-}$ (S$^{2-}$). On the other hand, a larger $a$-axis lattice parameter indicates that the Fe plane is stretched in K(Fe,Ag)$_2$Te$_2$ when compared to FeTe. The crystal structure of K(Fe,Ag)$_2$Te$_2$ is shown in Fig. 1(b), where antifluorite-type Fe/Ag-Te layers and K cation layers are stacked alternately along the $c$ axis. The XRD pattern of a single crystal [Fig. 1(c)] reveals that the crystal surface is normal to the $c$ axis with the plate-shaped surface parallel to the $ab$ plane. Figure 1(d) presents the EDX spectrum of a single crystal, which confirms the presence of the K, Fe, Ag, and Te. The average atomic ratios determined from EDX are K:Fe:Ag:Te = 1.00(3):0.85(2):1.15(2):1.0(1). The value of Fe/(Ag + Fe) determined from XRD fitting (0.38) is close to that obtained from EDX (0.43), which suggests that Te compound prefers to contain more Ag. This might explain why pure KFe$_2$Te$_2$ cannot form, since large Ag$^+$ ions have to be introduced in order to match the rather large Te$^{2-}$ anions and keep the stability of the structure. On the other hand, it should be noted that there are no K or Fe/Ag deficiencies in K(Fe,Ag)$_2$Te$_2$. This is rather different from K$_x$Fe$_{2-y}$Se$_2$ and K$_x$Fe$_{2-y}$S$_2$. Moreover, synchrotron powder X-ray
The big blue, small red, and medium orange balls represent K, Fe, or not more than 5% vacancies (i.e., Te). The EDX spectrum of a single crystal.

Figure 2 shows the temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ of the KFe$_{0.85}$Ag$_{1.15}$Te$_2$ single crystal for $H = 0$ (closed red circle) and 90 kOe (open blue square, $H||c$). Inset (a) shows the fitted result using thermal activation model for $\rho_{ab}(T)$ at zero field where the red line is the fitting curve. Inset (b) exhibits the temperature dependence of MR($T$) for KFe$_{0.85}$Ag$_{1.15}$Te$_2$.

TABLE I. Structural parameters for K(Fe,Ag)$_2$Te$_2$ at room temperature. Values in brackets give the number of equivalent distances or angles of each type. The occupancies of K and Te are fixed during fitting.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>$K_{x+y+z}$Fe$<em>{0.85}$Ag$</em>{1.52}$Te$_{2.01}$</th>
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<tr>
<td>space group</td>
<td>I4/mmm</td>
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<tr>
<td>$a$ (Å)</td>
<td>4.3707(9)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>14.9540(8)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>285.7(1)</td>
</tr>
<tr>
<td>Interatomic distances (Å) Bond angles (°)</td>
<td></td>
</tr>
<tr>
<td>$d_{Te-Ag/Te-Ag}$</td>
<td>3.0906(4) Te-Fe/Ag-Te [2] 104.44(3)</td>
</tr>
<tr>
<td>$d_{Te-Ag/Ag-Ag}$</td>
<td>2.7651(5) Te-Fe/Ag-Te [4] 112.05(4)</td>
</tr>
<tr>
<td>Anion heights (Å)</td>
<td>1.694(7)</td>
</tr>
<tr>
<td>Atom $x$ $y$ $z$ Occ. $U_{\text{iso}}$ (Å$^2$)</td>
<td></td>
</tr>
<tr>
<td>K 0 0 0 1.00 0.056(5)</td>
<td></td>
</tr>
<tr>
<td>Fe 0.5 0 0.25 0.76(8) 0.035(7)</td>
<td></td>
</tr>
<tr>
<td>Ag 0.5 0 0.25 1.24(8) 0.035(7)</td>
<td></td>
</tr>
<tr>
<td>Te 0.5 0.5 0.1367(5) 1.00 0.034(4)</td>
<td></td>
</tr>
</tbody>
</table>

The resistivity increases with decreasing temperature. Values in brackets give the number of equivalent distances or angles of each type. The occupancies of K and Te are fixed during fitting.

FIG. 1. (Color online) (a) Powder XRD patterns of KFe$_{0.85}$Ag$_{1.15}$Te$_2$. (b) Crystal structure of KFe$_{0.85}$Ag$_{1.15}$Te$_2$. The big blue, small red, and medium orange balls represent K, Fe/Ag, and Te ions. (c) Single-crystal XRD of KFe$_{0.85}$Ag$_{1.15}$Te$_2$. (d) The EDX spectrum of a single crystal.

The room-temperature value of $\rho_{ab}$ is about 2.7 Ω cm, which is much larger than in superconducting K$_x$Fe$_2$-Se$_2$ and semiconducting K$_x$Fe$_2$-S$_2$. The magnetic behavior might be related to the random distribution of Fe and Ag ions in the Fe/Ag plane which induces a random scattering potential, similar to the effect of Fe deficiency in the FeSe or FeS plane. By fitting the resistivity $\rho_{ab}(T)$ at high temperature using the thermal activation model $\rho = \rho_0 \exp(E_a/\kappa_B T)$, where $\rho_0$ is a prefactor and $\kappa_B$ is Boltzmann’s constant [inset (a) of Fig. 2], we obtained $\rho_0 = 71(6)$ mΩ cm and the activation energy $E_a = 96(2)$ meV in the temperature range above 200 K, which is larger than that of K$_x$Fe$_2$-Se$_2$K$_x$Fe$_{0.85}$Ag$_{1.15}$Te$_2$ exhibits large magnetoresistance $\text{MR} = (\rho(H) - \rho(0))/\rho(0)$ below about 100 K where the shoulder appears. As shown in inset (b) of Fig. 2, the negative MR is about 30% at 1.9 K for $H = 90$ kOe. This behavior is distinctly different from K$_x$Fe$_{2−}$-Se$_2$, which does not show any MR in measured temperature range.

Figure 3(a) presents the temperature dependence of magnetic susceptibility $\chi(T)$ of the KFe$_{0.85}$Ag$_{1.15}$Te$_2$ single crystal for $H = 1$ kOe along the $ab$ plane and the $c$ axis below 300 K with zero-field-cooling (ZFC) and field-cooling (FC). The $\chi_{ab}(T)$ is slightly larger than $\chi_{c}(T)$, and above 50 K, both can be fitted very well using Curie-Weiss law $\chi(T) = \chi_0 + C/(T - \theta)$, where $\chi_0$ includes core diamagnetism, van Vleck and Pauli paramagnetism, C is the Curie constant, and $\theta$ is the Curie-Weiss temperature [solid lines in Fig. 3(a)]. The fitted parameters are $\chi_0 = 5.46(7) \times 10^{-6}$ emu g$^{-1}$ Oe$^{-1}$, $C = 2.58(3) \times 10^{-3}$ emu g$^{-1}$ Oe$^{-1}$ K, and $\theta = -82(1)$ K for $\chi_{ab}$, and $\chi_0 = 3.5(1) \times 10^{-6}$ emu g$^{-1}$ Oe$^{-1}$, $C = 2.92(5) \times 10^{-3}$ emu g$^{-1}$ Oe$^{-1}$ K, and $\theta = -100(2)$ K for $\chi_{c}$. The above values of $C$ correspond to an effective moment of $\mu_{\text{eff}} = 3.60(2)$ μB/Fe and 3.83(3) μB/Fe for $\chi_{ab}$ and $\chi_{c}$, respectively. The values of $\mu_{\text{eff}}$ are smaller than for free Fe$^{2+}$ ions (4.7 μB/Fe) and Fe$_{1+x}$Te$_2$ (4.9 μB/Fe), but slightly larger than in K$_x$Fe$_{2−}$-Se$_2$ (3.31 μB/Fe).
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FIG. 3. (Color online) (a) Temperature dependence of DC magnetic susceptibility\( \chi(T) \) with the applied field \( H = 1 \text{kOe} \) along the \( ab \) plane and \( c \) axis below 300 K under ZFC and FC mode. The inset shows the \( d(\chi(T))/dT \) result for both field directions. (b) Isothermal magnetization hysteresis loops \( M(H) \) for \( H||ab \) and \( H||c \) at various temperatures.

We observe sharp drops below 35 K in both ZFC and FC curves, associated with the onset of long-range AFM order. The \( T_N = 35 \text{ K} \) is determined from the peak of \( d(\chi(T))/dT \) [inset of Fig. 3(a)]. It should be noted that antiferromagnetism below 35 K and Curie-Weiss paramagnetism at higher temperature are obviously different from \( \text{KFe}_2x\text{Se}_2 \) and \( \text{KFe}_2y\text{Se}_2 \). Figure 3(b) shows the magnetization loops for both field directions at various temperatures. It can be seen that all M-H loops exhibit almost linear field dependence and the \( M(H) \) curve exhibits a very small hysteresis at 1.8 K with a small coercive field (\( \sim 260 \text{ Oe} \)).

Figure 4 shows the temperature dependence of heat capacity \( C_p \) for \( \text{KFe}_{0.85}\text{Ag}_{1.15}\text{Te}_2 \) single crystals measured between \( T = 1.95 \) and 300 K in a zero magnetic field. At high temperature heat capacity approaches the Dulong-Petit value of \( 3.11(2) \text{ mJ mol}^{-1} \text{ K}^{-1} \). The obtained \( S_{\text{mag}}(T) \) can be calculated using the integral \( S_{\text{mag}}(T) = \int_0^T C_{\text{mag}}/dT \). Because of the failure of the Debye model at \( T > \Theta_D \), we estimated the lattice specific heat by fitting a polynomial to the \( C_p(T) \) curve at temperatures well away from \( T_N \). The obtained \( S_{\text{mag}} \) is about 2.4 J (mol Fe)\(^{-1} \text{ K}^{-1} \) up to 60 K, which is only 18% of theoretical value (\( 13.4 \text{ J (mol Fe)}^{-1} \text{ K}^{-1} \) for high-spin-state Fe\(^{2+} \) ions). Note that only about 1 J (mol Fe\(^{2+} \) K\(^{-1} \) is released below \( T_N \). This discrepancy may originate from an incorrect estimation of the lattice contribution to \( C_p(T) \), which can lead to reduced \( S_{\text{mag}}(T) \) or a probable short-range order that may exist above the bulk three-dimensional AFM order occurring at \( T_N \). This could also be supported by a much smaller \( T_N = 35 \text{ K} \) compared to the Curie-Weiss temperature \( \theta = -100(2) \text{ K} \) for \( H||c \).

There are two origins which could induce the negative MR effect in semiconductors: the reduction in spin disorder scattering due to the alignment of moments under a field, and the reduction of the gap arising from the splitting of the up- and down-spin subbands. The existence of AFM interaction could be related to this negative MR effect. The
temperature where MR effect becomes obvious is consistent with the Curie-Weiss temperature $\theta$, which implies this MR effect could be related to the AFM interaction and due to the reduction in spin disorder scattering with field. When compared to K$_4$Fe$_2$−$_y$Se$_2$, substitution of Ag has an important influence on the magnetic and transport properties. It could reduce the exchange interaction between Fe atoms and thus suppress the $T_N$ of KFe$_{0.85}$Ag$_{1.15}$Te$_2$ significantly. On the other hand, because of the near absence of vacancies in KFeCuS$_2$ and similar valence between Cu and Ag, it is more meaningful to compare the physical properties between KFeCuS$_2$ and KFe$_{0.85}$Ag$_{1.15}$Te$_2$. The former has the larger $E_a$ and room-temperature resistivity than the latter. This could be due to the smaller ionic sizes of Cu and S when compared to Ag and Te, which might lead to the smaller orbital overlap increasing $E_a$ and resistivity. Both compounds exhibit Curie-Weiss law above 50 K and the fitted Curie-Weiss temperature $\theta$ is very close to the transition of KFe$_{0.85}$Ag$_{1.15}$Te$_2$. However, the transition of KFeCuS$_2$ is spin glasslike, in contrast to the long-range AFM order of KFe$_{0.85}$Ag$_{1.15}$Te$_2$. This implies that the distribution of Ag in KFe$_{0.85}$Ag$_{1.15}$Te$_2$ may be different from Cu in KFeCuS$_2$, which results in a different magnetic ground-state configuration with similar interaction strength.

In summary, we successfully synthesized the K$_{1.003}$Fe$_{0.85(2)}$Ag$_{1.15(2)}$Te$_{2.0(1)}$ single crystals with ThCr$_2$Si$_2$ structure, identical to K$_{0.8}$Fe$_2$−$_y$Se$_2$ at 600 K. Crystal structure and composition analysis indicate that there are no K, Fe/Ag, and Te vacancies within 3, 2, or 5 at. %, respectively. Transport, magnetic, and thermal measurements indicate that the KFe$_{0.85}$Ag$_{1.15}$Te$_2$ is a semiconductor with long-range AFM order below 35 K.

We thank John Warren for help with scanning electron microscopy measurements and Jonathan Hanson for help with x-ray measurements. Work at Brookhaven is supported by the US DOE under Contract No. DE-AC02-98CH10886 and in part by the Center for Emergent Superconductivity, an Energy Frontier Research Center funded by the US DOE, Office for Basic Energy Science.

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