Electronic thermoelectric power factor and metal-insulator transition in FeSb₂

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(Received 23 May 2012; published 14 September 2012)

We show that synthesis-induced metal-insulator transition (MIT) for electronic transport along the orthorhombic c axis of FeSb₂ single crystals has greatly enhanced electrical conductivity while keeping the thermopower at a relatively high level. By this means, the thermoelectric power factor is enhanced to a new record high $S^2\sigma \sim 8000 \mu W K^{-2} cm^{-1}$ at 28 K. We find that the large thermopower in FeSb₂ can be rationalized within the correlated electron model with two bands having large quasiparticle disparity, whereas MIT is induced by subtle structural differences. The results in this work testify that correlated electrons can produce extreme power factor values.

DOI: 10.1103/PhysRevB.86.115121 PACS number(s): 72.20.Pa, 71.27.+a, 71.30.+h, 72.80.Sk

I. INTRODUCTION

The efficiency of thermoelectric (TE) material at temperature $T$ is evaluated by the figure of merit $ZT = (S^2/\rho\kappa)T$, where $S$ is the thermopower, $\rho$ is the electrical resistivity, and $\kappa$ is the thermal conductivity. There are two distinct approaches to increasing the $ZT$: either by $\kappa$ reduction or by power factor ($S^2/\rho$) enhancement. Techniques such as alloying, "phonon glass electron crystal" (PGEC) approach, and nanostructure engineering have been used to reduce the phonon mean free path, reduce lattice $\kappa$, and produce high $Z$, at or above the room temperature.¹–⁵ Reduction of the phonon mean free path has limitations since it cannot be reduced below the interatomic spacing and therefore other mechanisms for high $ZT$ are sought after.⁶ Tuning the carrier density by doping is often inadequate since lower $\rho$ comes with higher carrier concentration that favors lower $S$.⁷

The most favorable TE electronic structure is the one that has a resonance in the density of states centered about $\epsilon_F$ away from the Fermi energy ($\epsilon_F$).⁸ Kondo insulators (KI) represent a close approximation of such an ideal case. In a strongly correlated electron system, and, in particular, in a KI, localized $f$ or $d$ states hybridize with conduction electron states leading to the formation of a small hybridization gap. The density of states just below and just above the $\epsilon_F$ can be expected and are reported in KI.⁹ The materials include not only rare-earth-based compounds but also FeSi.¹⁰–¹⁵

FeSb₂ crystallizes in $Pmmm$ orthorhombic structure and has been characterized as an example of a strongly correlated noncubic Kondo insulator-like material with 3$d$ ions.¹⁶–¹⁸ Similar to FeSi, heavy fermion states were discovered in FeSb₂ by doping-induced metallization.¹⁹,²⁰ Colossal values of thermopower up to $\sim 45 \text{mV} K^{-1}$ at $10 \text{K}$ and a record high thermoelectric power factor (TEPF) of $\sim 2300 \mu W K^{-2} cm^{-2}$ were observed.²¹ This is two orders of magnitude larger than in best Bi₂Te₃-based materials and one order of magnitude larger than any reported value in correlated electron systems. Crystals in Refs. 19 and 21 exhibit semiconductor behavior and small resistivity anisotropy with relatively high resistivity for current directed along all three principal crystalline axes. In contrast, single crystals used in Kondo insulator studies showed high anisotropy of the resistivity: electric transport along the $a$ and $b$ axes is semiconducting, while the $c$ axis is metallic at high temperatures and exhibits metal-insulator transition (MIT) at $40 \text{K}$.¹⁶,¹⁷,²²

Here we investigated the TPF in two FeSb₂ crystals, with (crystal 1) and without (crystal 2) MIT. We show that large $S$ enhancement can be attributed to electronic correlations in multiple charge and heat carrying bands. We also provide evidence for structural origin of MIT in correlated electron bands that reduces $\rho$ by several orders of magnitude around $30 \text{K}$ in crystal 1 and results in a new record high TPF.

II. EXPERIMENT

Single crystals of FeSb₂ with MIT have been prepared as in Refs. 16 and 17 by decanting at $650 \text{°C}$. Single crystals of FeSb₂ without MIT have been prepared by the method described in Refs. 19 and 21, i.e., by decanting at $690 \text{°C}$, after a cool down from high temperatures to $640 \text{°C}$. Crystals were oriented using a Laue camera and cut into $0.5 \times 0.5 \times 5 \text{mm}$ samples for two probe thermopower measurements with two ends soldered on disk-shape leads using indium. Resistivity $\rho(T)$ was determined by a standard four-point ac method. Heat and current transport along the orthorhombic $c$ axis were measured using the Quantum Design PPMS platform. A magnetic field was applied along the crystallographic $a$ axis. Sample dimensions were measured with an optical microscope Nikon SMZ-800 with $10 \mu \text{m}$ resolution. Consequently the relative errors on the electrical resistivity and thermal conductivity are 4% and for the Hall coefficient, 2%. Since the Seebeck coefficient does not depend on the sample geometry the main source of error is the sample uniformity and the accuracy of crystal orientation which introduces the measurement error of up to 5%.

The atomic pair distribution (PDF) method, based on the total scattering approach, yields structural information on different length scales.²³ X-ray scattering experiments for PDF analysis were carried out at the 11-ID-C beamline of the Advanced Photon Source using high energy beam ($E = 114.82 \text{keV}$, $\lambda = 0.108 \text{Å}$, $0.5 \text{mm} \times 0.5 \text{mm}$ size). Both PDF, $G(r)$, and its algebraic relative, radial distribution function (RDF), $R(r)$, were considered in this study. Experimental PDF, $G(r)$ is obtained from the measured reduced total scattering structure factor, $F(Q) = Q[S(Q) - 1]$, via sine Fourier transform.
$G(r) = G(r) = (2/\pi) \int_0^\infty [F(Q) \sin(Qr)dQ]$. In practice, the upper limit of integration is some finite value $Q_{\text{max}}$. RDF, $R(r)$ is obtained from $G(r)$ through $R(r) = rG(r) + 4\pi r^2 \rho_0$, where $\rho_0$ is the average number density. Experimental setup for total scattering x-ray experiments utilized a Cryo Industries of America cryostat and Perkin-Elmer image plate detector. Finely ground samples in cylindrical polyimide capillaries were placed in a low-temperature sample changer, and the data for the two samples were successively collected for 4 min at each temperature in probed range between 5 and 300 K. PDFs were obtained up to $Q_{\text{max}} = 26 \text{ Å}^{-1}$ momentum transfer using standard protocols, and intermediate length scale structure modeled over (1.7–45.0) Å range with Pimm structural model using the program PDFGUI. Preliminary reference neutron total scattering based PDF’s were obtained using a time-of-flight HIPD instrument at Los Alamos Neutron Scattering Center.

III. RESULTS AND DISCUSSIONS

The $\rho_c$ for crystal 1 is metallic down to the onset of MIT ($T_{\text{MIT}}$), as opposed to crystal 2 [Fig. 1(a)]. Above 80 K and up to 300 K, $\rho_c(T)$ of crystal 2 is insensitive to magnetic field and is semiconducting. Interestingly, the logarithmic derivative, $d[\ln \rho_c(T)]/dT$ reveals an underdeveloped anomaly at $T_{\text{MIT}}$ in crystal 2 which points to the intrinsic nature of this temperature scale [Figs. 1(b) and 1(c)]. Arrenius analysis assuming thermally activated behavior leads to a number of distinct energy scales valid for limited subranges of this temperature interval (Table I), allowing only approximate estimation of the gap values. The absolute value $|d[\ln \rho_c(T)]|/dT$ in the metallic and insulating states is very similar, which is reminiscent of the universality observed near the MIT in low-dimensional electron gas systems. Below 5 K electrical transport is dominated by extrinsic impurity states and is governed by a very small activation gap, similar for both crystals. Distinct energy scales and indirect gaps are in agreement with optical spectroscopy studies and ab initio calculations. The large activation gap observed above 80 K in crystal 2 is not observed in the metallic phase of crystal 1, but its size argues against contribution of impurity states.

The Hall resistivity $\rho_{xy}(B)$ (current flowing along the $c$ axis) for both crystals [Figs. 2(a) and 2(b)] is nonlinear, confirming the presence of two carrier bands. In the absence of skew scattering we proceed to the analysis of the data in the two-band picture. In a two-carrier system

$$
\rho_{xy} = \frac{\rho_{xy}}{H} = \frac{\rho_0(\alpha_2 + \beta_2 H^2)/1 + \beta_2 H^2}{\alpha_2 f_1 \mu_1 + f_2 \mu_2, 2}, \quad \beta_2 = (f_1 \mu_2 + f_2 \mu_1) \mu_1, \quad \text{and} \quad \beta_1 = (f_1 \mu_2 + f_2 \mu_1) \mu_1,
$$

where $\rho_0 = \rho(B = 0)$, $f_1 = |n_1 \mu_1| / (\Sigma |n_i \mu_i|)$ is the $f$ factor, and $n_1$ and $\mu_1$ are individual carrier band concentrations.
and mobilities. The agreement with the model is excellent and we obtain carrier band concentrations and mobilities for crystal 2 while also showing data for crystal 1 for comparison. In the model "carrier" denotes a set of carriers with identical mobility associated with only one energy and/or one degenerate energy level and is different from the conventional electron or hole carriers that correspond to a continuous energy band. The low mobility carriers in crystal 2 are hole type \[\mu(2) \sim 10 \text{ cm}^2/\text{V s}\] and they are an order of magnitude less mobile when compared to hole carriers in crystal 1 at 300 K. Note that hole carriers in crystal 1 at room temperature constitute high mobility band \[\mu(1) \sim 10^2 \text{ cm}^2/\text{V s}\]. Yet, just like \(\mu(1)\), the \(\mu(2)\) band exhibits sign change below 50 K, having identical temperature dependence when compared to \(\mu(1)\) with up to three orders of magnitude lower nominal values. The \(\mu(2)\) carriers are electron type in crystal 2. They show little change in magnitude and do not change sign. The most striking difference between crystals 1 and 2 is the ratio of nominal mobility values. The large mobility difference is absent in crystal 2. Moreover, there is about or less than one order of magnitude between \(\mu(2)\) and \(\mu(2)_L\) in the high thermopower region from 10 to 40 K. The low and high carrier concentrations in both crystals have nearly identical values, suggesting a compensated nature of electronic transport at all temperatures. The carrier concentrations \(n_2(H)\) and \(n_2(L)\) are rather close at 300 K but they are both about an order of magnitude lower and have the same temperature dependence as carrier concentrations \(n_1(H)\) and \(n_1(L)\) in crystal 1. Carrier concentrations in crystals 1 and 2 are nearly identical in the temperature region of high thermopower, whereas in the impurity regime below 10 K crystal 2 (no MIT) shows much higher carrier concentrations. Values of carrier mobilities for crystal 2 (~10\(^{-3}\) cm\(^2\)/V s) are in general agreement with mobility values at low temperatures obtained using a two-band model (4–25 K) on crystals with no MIT.

Using carrier concentrations and Hall mobilities from a large number of measured \(\rho_{xy}(B)\) isotherms we obtain \(S(T)\) for both crystals in a two-band noninteracting semiconductor model where thermopower \(S = (S_e + S_h)/(\sigma_e + \sigma_h)\) and

\[
S_{e,h} = (k_B/e) \left[ \left\{ (S/2) + s \right\} F_{(3/2)+s}(\xi_{e,h}) - \xi_{e,h} \right],
\]

where \(F_j(\xi) = \int_0^\infty \frac{x^j dx}{\exp x + 1}\). The scattering exponent \(s\) represents the energy dependence of the relaxation time \(\tau = \tau_0 e^{\xi}\), \(\xi = \epsilon_F/(k_B T)\) are the reduced Fermi energies for electrons and holes \(\xi_e\) and \(\xi_h\) (as measured from the bottom of the conduction band for electrons and from the top of the valence band for holes), and \(\epsilon_F = h^2/(2m^* N/V)^{1/3}(3/8\pi)^{2/3}\). Hence, for semimetals \(\epsilon_{Fe} = -\epsilon_{Fh} + \epsilon_0\) and \(\xi_e = -\xi_h - \xi_0/(k_B T)\), where \(\epsilon_0\) is the overlap energy, and for semiconductors \(\epsilon_{Fe} = -\epsilon_{Fh} + \epsilon_0\) and \(\xi_e = -\xi_h - \xi_0/(k_B T)\), where \(\epsilon_0\) is the energy gap for semiconductors. In this model we used value \(s = -1/2\) assuming that acoustic phonon scattering is dominant at all temperatures and \(m^* = m_e\). The two-band noninteracting semiconductor model adequately describes crystal 2 above 50 K and below 5 K, whereas it fails to explain \(|S(T)|\) for crystal 1 in its metallic state (Fig. 3). While the similar shape of calculated and measured thermopower for both crystals between 10 and 40 K in the noninteracting model argues in favor of the two-band approach, such calculation does not explain the amplification of \(|S(T)|\) observed in the (10–30) K range. The prime suspect for discrepancy is strong correlations, which can have a significant impact on carriers in 3d bands.

In a correlated electronic system with two bands separated by a gap, \(S\) depends not only on the gap size but also on the anisotropy or asymmetry in the transport function:

\[
S = \frac{1}{|e|T} \left( \epsilon_F - \frac{\Delta}{2} - \frac{\delta \lambda}{2} \right) - \frac{5k_B}{2|e|} \delta \lambda,
\]

where \(\epsilon_F\) is the chemical potential, \(\Delta\) is the gap, and \(\delta \lambda = \lambda_0 - \lambda_s\) is the asymmetry parameter. The asymmetry parameter carries the information on band specific correlation strengths since \(\lambda_0 = Z_c \epsilon_{Fe} m_{c,v}^*/e - e^{\beta \mu}/T c_{c,v} m_{c,v}^*\), where \(Z_{c,v}\) are quasiparticle weights, \(\Gamma_{c,v}\) are scattering amplitudes, and \(m_{c,v}^*\) is the effective mass of carriers in conduction and valence bands. In addition, in real materials the \(|S(T)|\) rapidly diminishes with the increase in impurity concentration due to the increase of scattering amplitude, as recently observed in FeS\(_2\). Finally, the presence of impurities can have considerable effect on both \(|S(T)|\) and \(S(T)\). The \(S(T)\) magnitude at a given temperature depends on the ability of impurity carriers to put the Fermi level in the optimal position for thermopower enhancement. Both crystals have similar \(S(T)\) and nearly identical magnetothermopower \(\text{MT} = |S(9T) - S(0)|/|S(0)|\) in the region of high \(S\) (Fig. 3). In contrast to differences in \(\mu(T)\), thermopower \(S(T)\) for heat flow along the \(c\) axis is rather similar above 120 K and below 8 K. Thermopower changes sign from positive to negative above 100 K in both crystals, indicating the presence of two carrier types. Since \(m_{c,v}^* = e \tau_{c,v} / \mu_{c,v}\),

FIG. 3. (Color online) (a) \(|S(T)|\) for FeS\(_2\) crystals 1 (red) and 2 (blue squares). Red and blue balls show fits to the two-band noninteracting semiconductor model. Fits to the correlated electron model for crystal 1 are shown by red, purple, and brown (crystal 1) and dark blue, light blue, and violet (crystal 2) solid lines that correspond to increasing values of fixed energy gap \(\Delta\) (see text). The ratio of individual band mobilities in a two-carrier model is shown by the red/orange (crystal 1) and dark/light blue squares (crystal 2).
where $\tau_{c,v}$ is the scattering time and $\mu_{c,v}$ is the mobility in conduction and valence bands, we use mobility values for individual bands obtained from the fits of the $R_H$ in the two-band model. The value of $Z^2+5/2/\Gamma$ then becomes a fit parameter for each carrier band, in addition to the chemical potential $\epsilon_F$. Fits to the above equation for a fixed value of the gap which corresponds to the correlated electron temperature region (10–30 K) are shown in Fig. 3(a) as red (crystal 1) and blue (crystal 2) solid lines. The best fits are obtained for the gap values of $\sim$15–20 meV (Table I), suggesting that the large enhancement of $S$ gap values of blue (crystal 2) solid lines. The best fits are obtained for the region (10–30) K are shown in Fig. 3(a) as red (crystal 1) and $\lambda_{c,v}$ where $\epsilon_F$ and $\lambda_{c,v}$ (symmetric multiband effects) $S \rightarrow 0$. This is observed: $S$ sign change is at $T = (120 \pm 4)$ K, for both crystals 1 and 2. This implies that correlation effect on $S(T)$ vane at high temperatures.

The phonon drag is unlikely to have a significant contribution to $S$ since isostructural RuSb$_2$ and FeAs$_2$ have larger $\kappa$ and much smaller values of $[S(T)]_{\text{max}}$ due to different temperature dependence of $S$ and Nernst coefficient. $\tau_{c,v} \neq 0$. This is provided by a small number of mobile holes, which implies metallic conductivity and the MIT in crystal 1 which is the key for colossal TPF. For a large concentration of impurities the chemical potential can go into the valence/conduction band, producing metallic $\rho(T)$. While an order of magnitude disparity in the number of charge carriers observed in crystals 1 and 2 above $\sim$100 K would be consistent with such a scenario, it cannot be reconciled with the closely compensated nature of the carrier content. Below 10 K, where conductivity is governed by impurities, there are more carriers in crystal 2 than in crystal 1. Finally, impurity bands cannot account for the quasi-1D metallic conductance. Band structure suggests that the likely origin of the quasi-1D transport is the nonbonding $d_{xy}$ band, where the overlaps of Fe $d_{xy}$ orbitals are along the chains of edge-sharing octahedra parallel to the $c$ axis, with little or no overlaps between orbitals in different chains $\rho(T)$.27,40,41 Hall data shows that quasi-1D metallic conductance in sample 1 at temperatures above 40 K is provided by a small number of mobile holes, which implies a nearly filled valence band. Such a nonbonding band must be narrow and strongly correlated, and should be described valence-band carriers in two crystals show strikingly similar temperature dependence with a pronounced anomaly at MIT. Most importantly, in both cases there is a change in the nature of valence charge carriers, which are holes at temperatures above MIT and electrons at lower temperatures. As we discuss later, this observation reveals the likely nature of the MIT and of its absence in crystal 2.

Now we turn to the quasi-one-dimensional (quasi-1D) metallic conductivity and the MIT in crystal 1 which is the key for colossal TPF. For a large concentration of impurities the chemical potential can go into the valence/conduction band, producing metallic $\rho(T)$. While an order of magnitude disparity in the number of charge carriers observed in crystals 1 and 2 above $\sim$100 K would be consistent with such a scenario, it cannot be reconciled with the closely compensated nature of the carrier content. Below 10 K, where conductivity is governed by impurities, there are more carriers in crystal 2 than in crystal 1. Finally, impurity bands cannot account for the quasi-1D metallic conductance. Band structure suggests that the likely origin of the quasi-1D transport is the nonbonding $d_{xy}$ band, where the overlaps of Fe $d_{xy}$ orbitals are along the chains of edge-sharing octahedra parallel to the $c$ axis, with little or no overlaps between orbitals in different chains $\rho(T)$.27,40,41 Hall data shows that quasi-1D metallic conductance in sample 1 at temperatures above 40 K is provided by a small number of mobile holes, which implies a nearly filled valence band. Such a nonbonding band must be narrow and strongly correlated, and should be described

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FIG. 4. (Color online) The low resistivity around MIT leads to a record high TPF. Crystal 1 has two orders of magnitude higher TPF between 8 and 100 K.
by the 1D Hubbard model. The low-dimensional transport in such band is sensitive to disorder and MIT is expected at half filling. Can it be the origin of the MIT observed in crystal 1 that \( d_{xy} \) band is depleted with the decreasing temperature, attaining half-filling at \( T_{\text{MIT}} \)? Could it then be that a small additional disorder in crystal 2 induces localization of the quasi-1D charge carriers?

In order to answer this question, we performed the PDF analysis of the x-ray data taken on powder samples of crystals 1 and 2 (Figs. 5 and 6). The PDF provides insight into the crystal structure on short and intermediate length scales and allows quantifying subtle structural features such as bond properties and local disorder. Intrachain and interchain Fe-Sb-Fe angles, \( \beta_1(T) \) and \( \beta_2(T) \), respectively, shown in Fig. 5(b), are very similar, with a small difference developing in \( \beta_1 \) above 100 K. This may indicate charge redistribution involving \( d_{xy} \) bands since the presence of Fe \( d_{xy} \) charge will result in a somewhat larger \( \beta_1 \) angle. Atomic displacement factors (ADP) [Fig. 5(c)] of Fe atoms are rather anisotropic: mean-square atomic displacements along the \( a \) and \( b \) axes, \( U_{11} \) and \( U_{22} \), are nearly equal for both crystals, while those along the \( c \) axis, \( U_{33} \), are noticeably enhanced in crystal 2 at all temperatures, being 0.0084 \( \text{Å}^2 \) (crystal 2) and 0.0054 \( \text{Å}^2 \) (crystal 1) at 10 K. Enhanced ADPs are typical indication of disorder. In this case disorder is markedly 1D, precisely along the \( c \) axis and significantly higher in crystal 2.

It is clear from the difference curves (Fig. 6) in the x-ray RDF (Refs. 23 and 24) that the average local environments on the length scale of about one \( \text{Pmm} \) unit cell (reflected in the first several RDF peaks up to 4.5 \( \text{Å} \)) are indistinguishable. On larger length scales structural features start to differ. The RDF peak at about 4.65 \( \text{Å} \), denoted by a vertical arrow in Fig. 6, is markedly broader and less intense for crystal 2 at all temperatures studied. This peak corresponds to the next-nearest-neighbor Fe-Fe distance [FeSb\(_8\) interchain distance, double arrow in Fig. 5(a)], with no other contributions. Such a discrepancy could have several origins arising in a difference in Fe-Fe bond-length distribution, amount of Fe in the structures of the two crystals, charge state of Fe between the two crystals, or a combination of these effects.

Low-dimensional \( \rho \) is very sensitive to disorder which, in the simplest picture, suppresses metallic state by inducing strong localization. More generally, the disorder can impact the \( d_{xy} \) overlap and the band structure, the orbital character of the electronic states responsible for conduction, the occupancy of Fe \( d_{xy} \) orbitals, and even the orbital-dependent Hubbard \( U \) interaction strength in a \( d_{xy} \) quasi-1D band of itinerant states that forms with sufficient \( d_{xy} \) overlap. As opposed to this “self-generated” impurity level arising from Fe \( d \) orbitals in crystals with MIT, extrinsic impurity levels cannot produce metallic resistivity near or close to room temperature as in crystals with MIT and are significant only at low temperatures.

Crystals with MIT were cooled slowly from 1000 \( ^\circ\text{C} \) to 650 \( ^\circ\text{C} \) and were decanted at that temperature from the liquid Sb flux. On the other hand, crystals with no MIT were cooled to 640 \( ^\circ\text{C} \), closer to Sb solidification temperature and were subsequently decanted at 690 \( ^\circ\text{C} \). There are two main factors that could contribute to increased crystallographic disorder in crystals with no MIT: FeSb\(_2\) melts and decomposes at 738 \( ^\circ\text{C} \) to FeSb and Sb. Hence, crystallization occurs over a rather narrow temperature window. Crystals decanted at 690 \( ^\circ\text{C} \) are much closer to the melting point when compared to crystals decanted at 650 \( ^\circ\text{C} \). This could contribute to increased disorder in Fe-Sb chemical bonds. In addition, crystals cooled to 640 \( ^\circ\text{C} \) are closer to solidification line and are likely to experience more stress from the flux. This is consistent with observed structural differences, suggesting that MIT in FeSb\(_2\) crystals is governed by subtle structural differences tunable by synthesis procedure. Greatly increased conductivity near MIT, combined with significant electronic TEP, leads to a new record high thermoelectric power factor.

**IV. CONCLUSION**

In summary, we report the highest known TPF induced by the synthesis-controlled MIT in the correlated electron semiconductor FeSb\(_2\). The large thermopower enhancement can be understood within the electronic model, whereas MIT likely originates in quasi-1D and strongly correlated narrow bands of itinerant states very sensitive to disorder. This is further supported by the recent observation of quasi-1D magnetism in isostructural CrSb\(_2\).

**ACKNOWLEDGMENTS**

We thank T. M. Rice and Simon Billinge for useful discussions and Milinda Abeykoon and Pavol Juhas for help with x-ray experiments. This work was carried out at the Brookhaven National Laboratory, which is operated for the US Department of Energy by Brookhaven Science Associates DE-Ac02-98CH10886. The Advanced Photon Source at Argonne National Laboratory, operated by UChicago Argonne LLC, is supported under the US DOE-OS Contract No. DE-AC02-06CH11357. Neutron PDF experiments were carried out on HIPD at LANSCE, funded by DOE BES; LANL is operated by Los Alamos National Security LLC under DE-AC52-06NA25396.