Anisotropic magnetic and superconducting properties of $CaFe_{2-x}Co_xAs_2$ ($x=0$, 0.06) single crystals

Neeraj Kumar, R. Nagalakshmi, R. Kulkarni, P. L. Paulose, A. K. Nigam, S. K. Dhar, and A. Thamizhavel
Department of Condensed Matter Physics and Material Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India

(Received 5 October 2008; revised manuscript received 26 November 2008; published 22 January 2009)

We report on anisotropic dc magnetic susceptibility $\chi(T)$, electrical resistivity $\rho(T)$, and heat-capacity $C(T)$ measurements on the single crystals of $CaFe_{2-x}Co_xAs_2$ for $x=0$ and 0.06. Large-sized single crystals were grown by the high-temperature solution method with Sn as the solvent. The spin-density wave (SDW)/structural transition observed at 170 K in the pure $CaFe_2As_2$ compound is suppressed for the Co-doped sample $CaFe_{1.94}Co_{0.06}As_2$ and superconductivity is observed at $\simeq$17 K. The superconducting transition has been confirmed from the magnetization and electrical resistivity studies. The ^{57}Fe Mössbauer spectrum in $CaFe_2As_2$ indicates that the SDW ordering is incommensurate with the crystal lattice. In the Co-doped sample, a prominent paramagnetic line at 4.2 K is observed indicating a weakening of the SDW state.

DOI: 10.1103/PhysRevB.79.012504 PACS number(s): 74.25.Ha, 75.30.Fv, 75.10.Dg, 71.20.Dg

The discovery of superconductivity at a high transition temperature $T_c \approx 26$ K in iron-based $LaFeAsO_{1-x}F_x$ (Ref. 1) has created a torrent of research activities in the field of magnetism and superconductivity. T_c is significantly enhanced in these oxypnictides both by the application of external hydrostatic pressure[2] ($T_c \approx 43$ K at 4 GPa) and replacing La with smaller-sized rare-earth ions [$T_c \approx 43$ K in the isostructural compound $SmFeAsO_{1-x}F_x$ (Ref. 3)]. The crystal structure of these compounds is characterized by an alternative stacking of LaO and FeAs layers such as LaO-FeAs-LaO-FeAs, where the Fe and As atoms are strongly coupled by covalent bond.[2] Although the oxypnictides possess high superconducting transition temperature, crystal growth of a sizable amount has not been achieved until recently to understand the anisotropic physical properties and the nature of superconductivity. More recently, another class of FeAs-based compounds AFe_2As_2 (A=Ba, Ca, Sr, and Eu)[4–7] has been identified in which superconductivity can be induced either by doping or by applying hydrostatic pressure. For example, K (hole)-doped $Ba_{0.55}K_{0.45}Fe_2As_2$ shows a T_c as high as 38 K (Ref. 8) while Co (electron)-doped $BaFe_{1.8}Co_{0.2}As_2$ exhibits a superconducting transition at 22 K.[9] The crystal structure of AFe_2As_2 contains FeAs layers, similar to oxypnictides, which are separated by the layers of A atoms. Unlike the oxypnictides, the AFe_2As_2 compounds can be grown in single crystalline form by high-temperature solution growth method using either a Fe-As self-flux taking advantage of the Fe-As binary eutectic or with Sn as flux.

While new results are being reported at a fast pace, to our knowledge, the results of Co-doped single crystalline $CaFe_2As_2$ have not been reported until recently. In this Brief Report, we present our results on the anisotropic properties of pure and Co-doped single crystals of $CaFe_2As_2$. Single crystals of $CaFe_{2-x}Co_xAs_2$ ($x=0$ and 0.06) were grown by high-temperature solution growth using Sn as flux. The starting materials were high-purity metals of Ca, (Fe,Co), As, and Sn taken in the ratio of 1:2:2:19 for pure compound; for the Co-substituted sample our starting composition was 1:1.8:0.2:2:19. The contents were placed in a high-quality recrystallized alumina crucible and subsequently sealed in an evacuated quartz ampoule. The furnace was slowly heated to 1050 °C and held at that temperature for 24 h to ensure homogenization. It was gradually cooled down to 450 °C over a period of 3 weeks and then rapidly brought down to room temperature. The flux was removed by means of centrifuging. Very-large-sized single crystals with typical dimensions of $20\times12\times0.4$ mm^3 were obtained. Laue patterns showed that the c axis is normal to the flat plane of the crystal. The crystals were silvery white and malleable. Electron probe microanalysis showed that the composition of the Co-doped single crystal is $CaFe_{1.94}Co_{0.06}As_2$.

The phase purity of the single crystalline sample was confirmed by performing powder x-ray diffraction by grinding a few pieces of the single crystals. The x-ray pattern can be indexed to the $ThCr_2Si_2$-type body-centered tetragonal structure with the space group $I4/mmm$. The estimated lattice parameters are $a=3.894\,2(8)$ Å and $c=11.746(7)$ Å for $CaFe_2As_2$ and $a=3.887\,5(1)$ Å and $c=11.687(1)$ Å for $CaFe_{1.94}Co_{0.06}As_2$. The lattice parameter of the pure sample is in agreement with the previously reported values.[7,8] The Co doping compresses the c axis by 0.5% and the a axis by 0.17%.

Figure 1(a) shows the temperature dependence of the magnetic susceptibility of $CaFe_{1.94}Co_{0.06}As_2$ measured in a field of 0.5 T. For the sake of comparison the corresponding data of $CaFe_2As_2$ in an applied field of 5 T are shown in Fig. 1(b). A sharp drop [Fig. 1(b)] in the magnetic susceptibility at 170 K is a signature of a spin-density wave (SDW) magnetic ordering associated with the iron moments and a lattice structural transition in $CaFe_2As_2$. In this regard our data are in agreement with earlier reports in the literature.[7,10,11] In particular the magnitude of χ for $H\|[001]$ is nearly the same as of Ni *et al.*[10] The 170 K anomaly has vanished for the Co-doped sample indicating a suppression of the SDW ordering. However, the susceptibility of $CaFe_{1.94}Co_{0.06}As_2$ along [100] shows an anomaly near 90 K which may arise due to an antiferromagneticlike ordering of the residual Fe moments. Incidentally we see a similar feature along [100] around the same temperature in $CaFe_2As_2$, but not observed by others,[7,10,11] which may imply a reorientation of the Fe

 ©2009 The American Physical Society

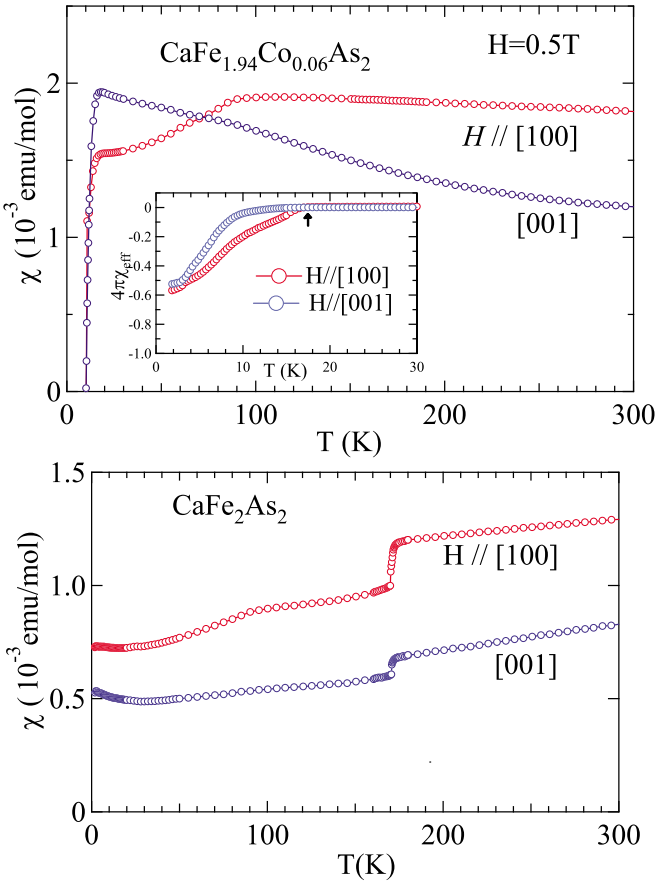

FIG. 1. (Color online) (a) Temperature dependence of magnetic susceptibility of $CaFe_{1.94}Co_{0.06}As_2$ in a field of 0.5 T. The inset shows the low-temperature part of the dc magnetic susceptibility measured in 0.005 T. The arrow at 17 K indicates the onset of diamagnetic susceptibility. (b) Temperature dependence of the magnetic susceptibility of $CaFe_2As_2$ for $H\|[100]$ and [001] in an applied magnetic field of 5 T.

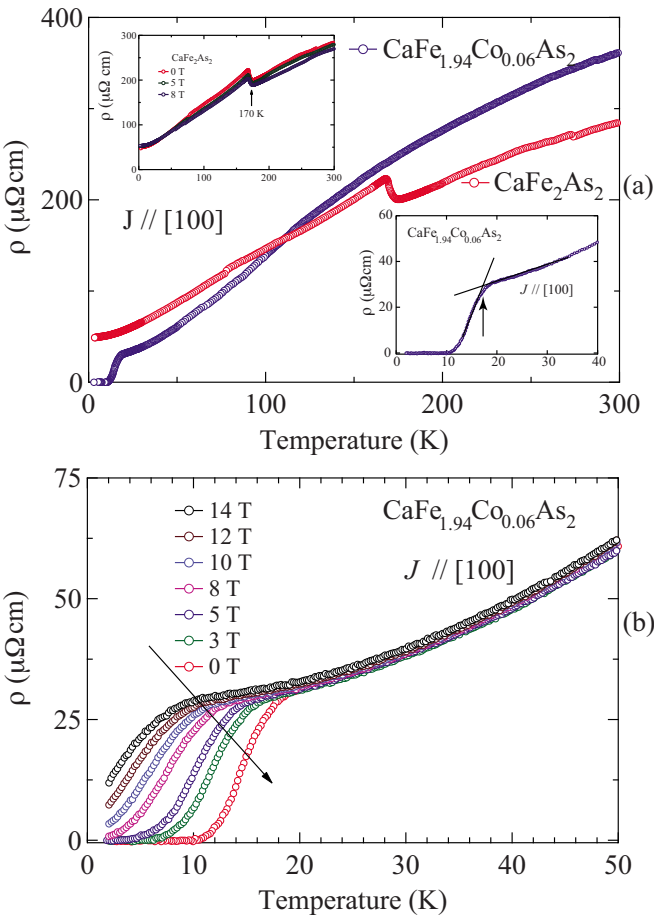

FIG. 2. (Color online) (a) Temperature dependence of the electrical resistivity of $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$ for $J\|[100]$; the upper inset shows the electrical resistivity of $CaFe_2As_2$ measured at 5 and 8 T and the lower inset shows the low-temperature part of the superconducting $CaFe_{1.94}Co_{0.06}As_2$ sample. The T_c in $CaFe_{1.94}Co_{0.06}As_2$ is found to be 17 K as shown in the lower inset. (b) Resistivity measured at various applied magnetic fields of $CaFe_{1.94}Co_{0.06}As_2$ for $J\|[100]$ and $B\|[001]$.

moments. At lower temperatures a sharp drop in the susceptibility near 17 K in $CaFe_{1.94}Co_{0.06}As_2$, attaining diamagnetic values with the decrease in temperature, is a signature of a superconducting transition. The inset of Fig. 1(a) shows the diamagnetic susceptibility, corrected for the demagnetization factor N for $H\|[001]$,[12] along both the principal directions measured in a field of 0.005 T. The superconducting volume fraction is found to be (55–60)%.

The temperature dependence of dc electrical resistivity from 1.8 to 300 K for both pure and Co-doped $CaFe_2As_2$ single crystals for current parallel to [100] direction is shown in Fig. 2(a). The magnitude and the thermal variation in the electrical resistivity of the pure compound are in agreement with the earlier reports.[7,10] The sharp increase near 170 K is due to the SDW/structural transition. The upper inset of Fig. 2(a) shows the electrical resistivity measured in 5 and 8 T for the pure $CaFe_2As_2$. It is evident that the magnetic field has virtually no effect on the electrical resistivity and that the SDW ordering is insensitive to the fields as high as 8 T. Our observation is in conformity with a similar conclusion arrived earlier by Ni *et al.*[10] who found the first-order phase transition at 170 K unaffected by fields as high as 14 T. On the other hand, the electrical resistivity of $CaFe_{1.94}Co_{0.06}As_2$ does not show any anomaly at 170 K in accordance with the susceptibility data presented above. It appears to vary smoothly across 90 K where the susceptibility along [100] shows an anomaly as discussed above. At 17 K the electrical resistivity drops rapidly and becomes zero at lower temperatures. The lower inset of Fig. 2(a) shows the onset of superconducting transition on an expanded scale. Figure 2(b) shows the temperature dependence of the electrical resistivity below 50 K of $CaFe_{1.94}Co_{0.06}As_2$ for the current parallel to [100] in various applied magnetic fields ($H\|[001]$). Data with current and field both parallel to [100] were also recorded and showed a similar trend. As the field is increased the transition becomes broader and T_c shifts to lower temperature which is a characteristic feature of a type-II superconductor. It may be noticed that we obtained a zero resistance state even in an applied field of 8 T, which indicates a high critical field H_{c2}. There is only a marginal change in the normal state resistivity with applied field.

Using the procedure depicted in the lower inset of Fig.

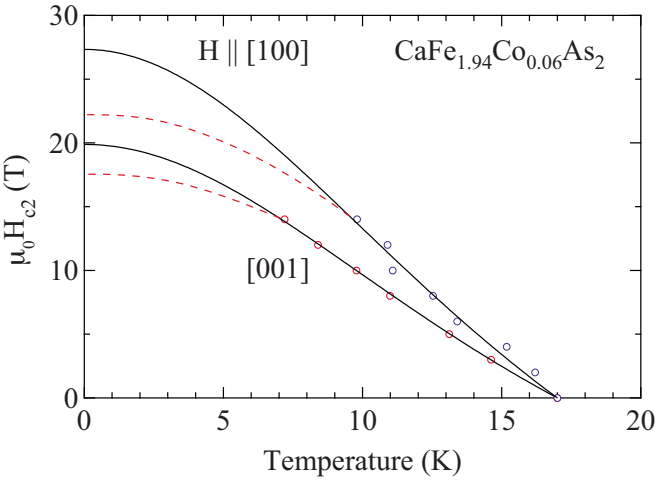

FIG. 3. (Color online) Temperature dependence of the upper critical field $\mu_0 H_{c2}(T)$ of $CaFe_{1.94}Co_{0.06}As_2$. The dashed line is the value of $\mu_0 H_{c2}$ estimated by WHH theory and the solid line is according to Ginzburg-Landau theory (see text for details).

2(a) we can determine the temperature dependence of the upper critical field H_{c2} which is plotted in Fig. 3. The variation in H_{c2} with temperature is nearly linear with a negative slope and it does not show any kind of saturation for fields as high as 14 T. However one can estimate $H_{c2}(0)$ by using the Werthamer-Helfand-Hohenberg (WHH) (Ref. 13) equation $H_{c2}(0) = -0.7 T_c (dH_{c2}/dT_c)$. The slope dH_{c2}/dT_c is estimated to be −1.82 T/K for $H \| [100]$ and −1.43 T/K for $H \| [001]$. For a T_c of 17 K, the upper critical field $H_{c2}(0)$ is found to be 22 and 17 T for $H \| [100]$ and [001] directions, respectively, as shown by the dotted line in Fig. 3. According to Ginzburg-Landau (GL) theory, H_{c2} can also be determined by using the formula $H_{c2} = H_{c2}(0)(1-t^2)/(1+t^2)$, where $t = T/T_c$ is the reduced temperature. The solid line in Fig. 3 gives a good fit to the above equation and $H_{c2}(0)$ value thus determined amounts to 27 and 20 T for $H \| [100]$ and [001] directions, respectively. These values are slightly larger than that ob-

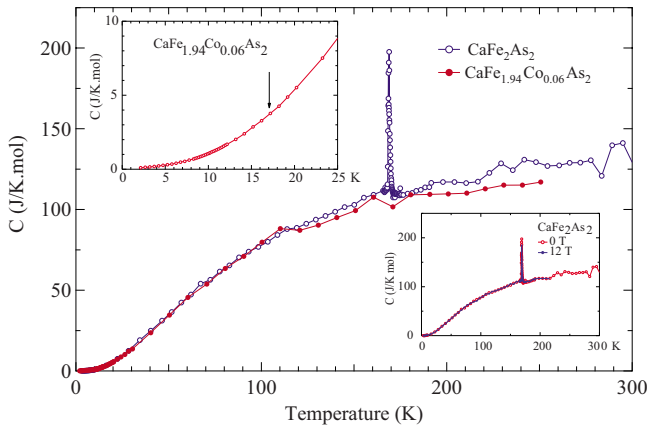

FIG. 4. (Color online) Temperature dependence of the heat capacity of $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$. The high-temperature SDW ordering is absent in the Co-doped sample. The lower inset shows the heat capacity of $CaFe_2As_2$ in 0 and 12 T fields. The upper inset shows the temperature dependence of the heat capacity of $CaFe_{1.94}Co_{0.06}As_2$ below 25 K.

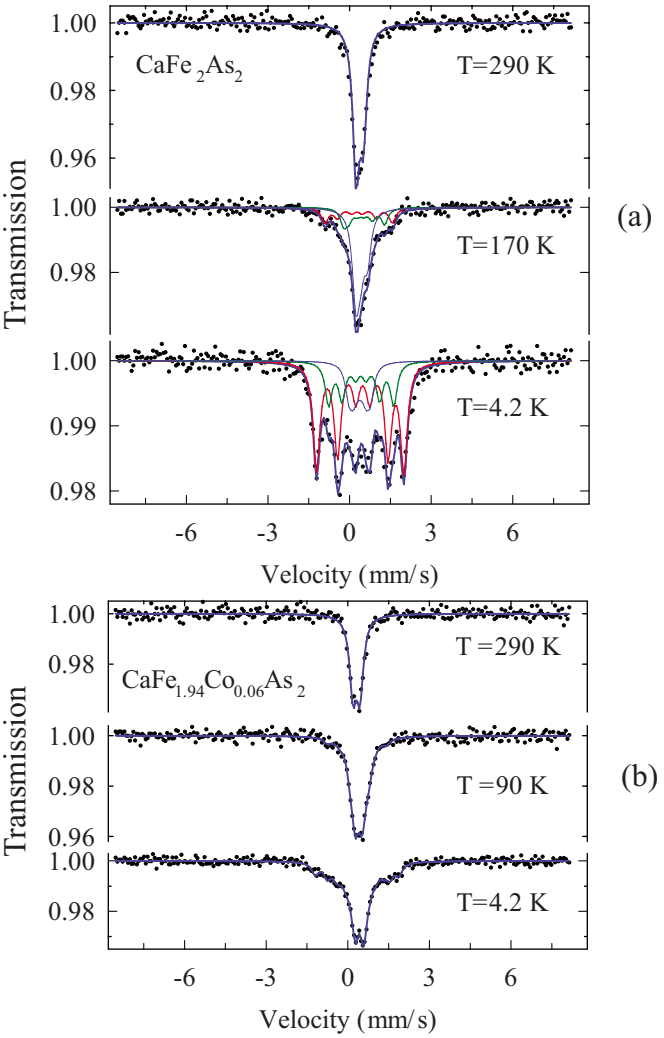

FIG. 5. (Color online) Mössbauer spectra of $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$ at selected temperatures. For $CaFe_2As_2$ the three subspectra at 4.2 K are shown (see text).

tained from WHH theory. Using the expression $\xi = \Phi_0/2\pi H_{c2}$ for the coherence length, where $\Phi_0 = 2.07 \times 10^{-7}$ Oe cm^2, we infer a coherence length of 40 Å.

Figure 4 shows the heat capacity from 1.8 to 300 K of $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$. A sharp peak at 170 K indicates a first-order-like transition for $CaFe_2As_2$ similar to the previous reports.[7,10] However, in the Co-doped sample the peak at 170 K has vanished, which is in correspondence with the susceptibility and the resistivity data. The heat-capacity data vary smoothly across 90 K but at slightly higher temperatures one can imagine that some kind of anomaly is present near 110 K. The top inset of Fig. 4 shows the heat capacity of $CaFe_{1.94}Co_{0.06}As_2$ below 25 K. The jump at T_c is not discernible from the heat-capacity data. Keeping in view the relatively broad superconducting transition as seen in both the susceptibility and resistivity, we believe that the anomaly in the heat capacity at T_c is broadened and submerged in the background phonon contribution. We may mention here that in $Ba_{0.55}K_{0.45}Fe_2AS_2$, where the superconducting transition is sharp, the anomaly in the heat capacity at T_c is barely discernible.[14] It may also be noted that the

heat capacity of pure and Co-doped samples (main panel) is almost similar. We infer that the Co doping at $x=0.06$ level leave the phonon spectrum virtually unchanged.

We have also measured the heat capacity of $CaFe_2As_2$ in a field of 12 T with the field direction parallel to both the crystallographic directions, namely, [100] and [001] (lower inset of Fig. 4). The magnetic field has virtually no effect on the SDW transition. It has been pointed out that in a magnetic field the spin-density wave couples with bands of opposite spin leaving the nesting unaffected.[15]

The magnetic state of Fe in $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$ was further investigated by recording ^{57}Fe Mössbauer spectra at selected temperatures (Fig. 5). The room-temperature spectra for both samples were quadrupole split ($eqQ/2=0.25$ mm/s) paramagnetic lines. In the pure compound the spectra are hyperfine field split below the SDW transition; the spectrum at 170 and 4.2 K is fitted to a Hamiltonian consisting of magnetic and quadrupolar terms. The best fit to the experimental spectrum was obtained by a superposition of three subspectra with negligible quadrupole splitting (<0.1 mm/s) corresponding to hyperfine fields of 10, 7.4, and 2.5 T with weightages of 60%, 24%, and 16%, respectively, at 4.2 K.

The occurrence of multiple subspectra with widely different hyperfine fields in the pure compound appears strange as there is only one Fe site in the crystal structure. One reason could be the possible modulation of the magnetic structure incommensurate with the crystalline lattice, giving rise to a hyperfine field distribution as reported in EuPdSb.[16] An incommensurate spin-density wave order has been proposed as the cause of inhomogeneous broadening of the ^{75}As NMR line in single crystal of $BaFe_2As_2$ grown from Sn flux, although the neutron scattering results find a commensurate order.[17] On the other hand a commensurate SDW ordering has been reported on a self-flux-grown single crystal of $BaFe_2As_2$ from ^{75}As NMR measurements.[18] It has been claimed that the presence of even small amount of Sn in the single crystal can have a large effect on NMR spectra. While our results indicate an incommensurate magnetic ordering, neutron diffraction on a single crystal of $CaFe_2As_2$ grown using Sn flux reveals a commensurate ordering.[8] We feel that the nature of SDW ordering needs further investigation.

Turning our attention to the Co-doped sample, the purely quadrupolar split, paramagnetic Mössbauer spectrum at room temperature persists down to about 100 K. At 90 K an additional feature characterized by a broadening in the wings is observed which progressively increases down to 4.2 K. Although it can arise due to relaxation effects, the anomaly at 90 K in the magnetization data suggests a magnetic origin of the broadening. The spectrum at 4.2 K can be simulated by a superposition of four subspectra corresponding to magnetic hyperfine fields of 9.5, 7.1, and 2.7 T with weightages of nearly 20% each and a predominant paramagnetic component of 40%. The Mössbauer data thus corroborate the weakening of the SDW with even a small amount of Co doping, leading to the emergence of a superconducting state. This is consistent with the high-pressure data[19,20] where even a relatively low pressure of 2 kbar is sufficient to induce superconductivity with a T_c of nearly 10 K.

To conclude, we have grown large-sized single crystals of $CaFe_2As_2$ and $CaFe_{1.94}Co_{0.06}As_2$ by flux method using Sn as flux. Our ^{57}Fe Mössbauer results indicate that the SDW ordering in $CaFe_2As_2$ is incommensurate. Co doping at the Fe site reduces the unit-cell volume marginally and it weakens the SDW ordering and induces superconductivity at a relatively high temperature of 17 K. The upper critical field is estimated to be 20 T.

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature (London) **453**, 376 (2008).
[3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) **453**, 761 (2008).
[4] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pottgen, Phys. Rev. B **78**, 020503(R) (2008).
[5] J. Q. Yan, A. Kreyssig, S. Nandi, N. Ni, S. L. Budko, A. Kracher, R. J. McQueeney, R. W. McCallum, T. A. Lograsso, A. I. Goldman, and P. C. Canfield, Phys. Rev. B **78**, 024516 (2008).
[6] Z. Ren, Z. Zhu, S. Jiang, X. Xu, Q. Tao, C. Wang, C. Feng, G. Cao, and Z. Xu, Phys. Rev. B **78**, 052501 (2008).
[7] F. Ronning, T. Klimczuk, E. D. Bauer, H. Volz, and J. D. Thompson, J. Phys.: Condens. Matter **20**, 322201 (2008).
[8] A. I. Goldman, D. N. Argyriou, B. Ouladdiaf, T. Chatterji, A. Kreyssig, S. Nandi, N. Ni, S. L. Bud'ko, P. C. Canfield, and R. J. McQueeney, Phys. Rev. B **78**, 100506(R) (2008).
[9] A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus, Phys. Rev. Lett. **101**, 117004 (2008).
[10] N. Ni, S. Nandi, A. Kreyssig, A. I. Goldman, E. D. Mun, S. L. Bud'ko, and P. C. Canfield, Phys. Rev. B **78**, 014523 (2008).
[11] G. Wu, H. Chen, T. Wu, Y. L. Xie, Y. J. Yan, R. H. Liu, X. F. Wang, J. J. Ying, and X. H. Chen, J. Phys.: Condens. Matter **20**, 422201 (2008).
[12] R. Prozorov, R. W. Giannetta, A. Carrington, and F. M. Araujo-Moreira, Phys. Rev. B **62**, 115 (2000).
[13] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).
[14] N. Ni, S. L. Budko, A. Kreyssig, S. Nandi, G. E. Rustan, A. I. Goldman, S. Gupta, J. D. Corbett, A. Kracher, and P. C. Canfield, Phys. Rev. B **78**, 014507 (2008).
[15] R. H. McKenzie, arXiv:cond-mat/9706235 (unpublished).
[16] P. Bonville, J. A. Hodges, M. Shirakawa, M. Kasaya, and D. Schmitt, Eur. Phys. J. B **21**, 349 (2001).
[17] S.-H. Baek, T. Klimczuk, F. Ronning, E. D. Bauer, J. D. Thompson, and N. J. Curro, Phys. Rev. B **78**, 212509 (2008).
[18] K. Kitagawa, N. Katayama, K. Ohgushi, M. Yoshida, and M. Takigawa, J. Phys. Soc. Jpn. **77**, 114709 (2008).
[19] T. Park, E. Park, H. Lee, T. Klimczuk, E. D. Bauer, F. Ronning, and J. D. Thompson, J. Phys.: Condens. Matter **20**, 322204 (2008).
[20] M. S. Torikachvili, S. L. Bud'ko, N. Ni, and P. C. Canfield, Phys. Rev. Lett. **101**, 057006 (2008).