Journal of Alloys and Compounds 508 (2010) 606–609

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Electrical transport properties of F-doped LaFeAsO oxypnictide

Li-Dong Zhao[a,b,*], David Berardan[a,b], Nita Dragoe[a,b]

[a] Univ. Paris-Sud, Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, Orsay F-91405, France
[b] CNRS, Orsay F-91405, France

ARTICLE INFO

Article history:
Received 5 August 2010
Received in revised form 14 August 2010
Accepted 26 August 2010
Available online 28 September 2010

Keywords:
Thermoelectric
Oxyarsenide
Electrical transport properties
Spin-density-wave

ABSTRACT

A series of $LaFeAsO_{1-x}F_x$ ($x = 0$–0.225) oxyarsenides have been synthesized by a solid-state reaction method in order to optimize electrical transport properties through appropriate F doping. Both electrical resistivity and Seebeck coefficient of undoped LaFeAsO show an anomaly at about 150 K, which is related to a structural phase and/or spin-density-wave (SDW) transition. Seebeck coefficient seems to be determined by two competitive factors: it is enhanced by suppressing the structural phase and/or SDW transition, and reduced by increasing carrier concentration. Seebeck coefficient is significantly enhanced just after suppressing the anomaly, and the maximum Seebeck coefficient reached −142 μV/K for the sample with F doping $x = 0.075$ from −58 μV/K for undoped LaFeAsO, and then decreased with further increasing carrier concentration through F doping. Meanwhile, the electrical resistivity is decreased with increasing F doping, resulting in a maximum power factor value of 1.2 mW/mK^2 at 80 K for polycrystalline $LaFeAsO_{0.85}F_{0.15}$ sample, this value is the same order as that of the best low temperature thermoelectric $Bi_{88}Sb_{12}$ compounds, and could be significantly higher in single crystals.

1. Introduction

Thermoelectric (TE) power generators and refrigerators are solid-state devices without moving parts. They are silent, reliable and scalable, making them ideal for small, distributed power generation [1]. The conversion efficiency of TE devices is determined by the dimensionless figure of merit (ZT), defined as $ZT = (S^2/\rho k)T$, where S, ρ, k, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Therefore, high performance TE materials should have excellent electrical transport properties (S^2/ρ) and low thermal conductivity (k). Recently, much attention has been paid on the layered rare-earth iron oxypnictides *Ln*Fe*Pn*O (*Ln* = La, Pr, Ce, Sm and Nd; and *Pn* = P and As) with ZrCuSiAs tetragonal structure (space group: $P4/nmm$) since superconductivity has been discovered at $T_c = 26$ K in the iron-based $LaFeAsO_{1-x}F_x$ ($x = 0.05$–0.12) [2]. Following these surprising findings, Dragoe and his co-workers also found that iron-oxypnictides family, *Ln*FeAsO (*Ln* = La, Sm and Nd) with F doping, also exhibits large Seebeck coefficients with the order of −100 μV/K after appropriately doping, while keeping good electrical conductivity. Their power factor shows a peak at low temperatures, suggested possible applications of these materials in thermoelectric cooling modules in the liquid nitrogen temperature range [3]. Interestingly, the enhanced Seebeck coefficient usually appears with the onset of superconductivity in iron-oxypnictide superconductors [4–8]. It is well known that the superconductor usually shows excellent electrical conductivity. Hence, good thermoelectric transport properties could be expected with considering the emergence of enhanced Seebeck coefficient in iron-oxypnictides.

In this paper, a series of $LaFeAsO_{1-x}F_x$ oxyarsenide compounds with F doping on O site ($x = 0$–0.225) have been synthesized by a solid-state reaction method in order to enhance the electrical transport properties through optimizing F doping. The electrical resistivity and Seebeck coefficient of the resultant bulk samples were investigated with a special emphasis on the effects of F doped contents. The obtained results indicate that $LaFeAsO_{1-x}F_x$ iron-oxypnictides are promising thermoelectric materials applied in low temperature range.

2. Experimental

Samples with the chemical composition $LaFeAsO_{1-x}F_x$ ($x = 0$, 0.075, 0.15 and 0.225) were prepared by using a two-step solid-state reaction route. In the first step, LaAs was prepared by heating La and As chunks in a sealed silica tube under argon, at 600 °C for 2 h with a ramp-up speed of 50 °C/h, followed by 900 °C for 12 h with a ramp-up speed of 100 °C/h. The obtained alloy was single phase LaAs as confirmed by X-ray diffraction measurements. Then the LaAs alloy was thoroughly grounded together with Fe_2O_3 powder, FeF_2 powder and Fe powder in stoichiometric amount as given by the formula $LaFeAsO_{1-x}F_x$. The thoroughly mixed powders were pressed under 250 MPa to form 2 mm × 3 mm × 12 mm bars. The bars were wrapped in tantalum foils and sealed in a silica tube under argon, and then heated and reacted at 1150 °C for 50 h with a ramp-up speed of 100 °C/h. The sample preparation processes including weighing raw materials, grounding powders and pressing bars were carried out in a pure argon-filled glove box with less than 1 ppm O_2 and

---

[*] Corresponding author. Tel.: +33 169153193.
E-mail addresses: zhaolidong1979@163.com, lidong.zhao@u-psud.fr (L.-D. Zhao).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.08.138

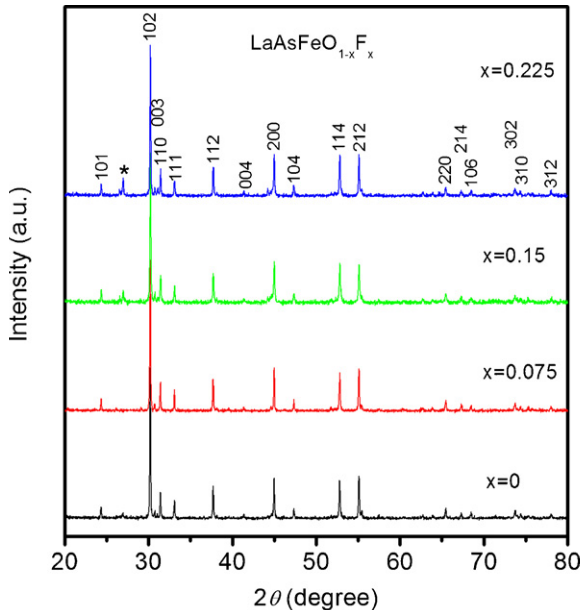

Fig. 1. X-ray powder diffraction patterns for LaFeAsO$_{1-x}$F$_x$ oxyarsenides.

H_2O. X-ray diffraction patterns were obtained using a Panalytical X'Pert with a Ge (1 1 1) incident monochromator and an X'celerator detector, with rotating sample. Rietveld refinement was performed using FullProf software [9]. Electrical resistivity was measured using a DC four wires method in a closed cycle cryostat, from 300 K to about 15 K. The Seebeck coefficient was measured by a method with two T-type thermocouples, by using the slope of the ΔV–ΔT curve with gradients up to about 0.2 K/mm, in a closed cycle cryostat from 300 K to about 20 K by using a laboratory made system. All transport measurements were performed in a direction perpendicular to the pressing direction.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized LaFeAsO$_{1-x}$F$_x$ samples. All the XRD peaks can be well indexed based on a tetragonal cell with space group *P*4/*nmm* indicating that the samples are almost single phase. However, it should be noted that the sample with the largest amount of F ($x = 0.225$) contains a few percent of impurity phases (LaOF).

Fig. 2 shows the temperature dependence of the electrical resistivity (ρ). The electrical resistivity for undoped LaFeAsO decreases slightly with decreasing temperature peaking at about 150 K, and then it decreases sharply with decreasing temperature. It should be noted that the electrical resistivity of undoped LaFeAsO show an anomaly at about 150 K, this phenomenon is similar to the reported LaFeAsO$_{1-x}$F$_x$ samples [10]. As reported before [11], this upturn in electrical resistivity is likely associated with a structural phase transition and/or an antiferromagnetic spin-density-wave (SDW) transition. It also can be considered as an increase of the charge-carrier scattering by lattice fluctuations related to the onset of the structural transition [12,13]. This anomaly cannot be observed after F doping, and the electrical resistivity for all F doped samples in the whole measuring temperature range decreases with increasing F doped contents up to 0.225. Reduction in electrical resistivity suggests that the carrier concentration has been increased by introducing electron through F$^-$ ionic doping on O^{2-} ionic site in LaFeAsO$_{1-x}$F$_x$ samples. The electrical resistivity for LaFeAsO$_{0.85}$F$_{0.15}$ and LaFeAsO$_{0.775}$F$_{0.225}$ samples decreases with decreasing the temperature, and shows a metallic-like transport properties. For comparison, the electrical resistivity of Bi$_{88}$Sb$_{12}$ [14], the best low temperature thermoelectric material, also was plotted in Fig. 1. It can be seen that all the LaFeAsO$_{1-x}$F$_x$ samples show the higher electrical resistivity than that of Bi$_{88}$Sb$_{12}$. However, it must be emphasized that the electrical resistivity measured in LaFeAsO$_{1-x}$F$_x$ is not so far from that of Bi$_{88}$Sb$_{12}$, as our samples are poorly densified (in this paper, the relative density for all the samples is about 60%), and that much lower electrical resistivity values can be expected for highly dense samples and single crystals.

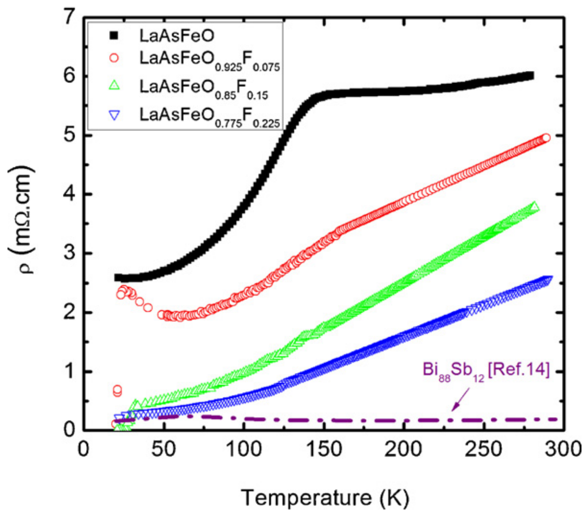

Fig. 2. Electrical resistivity of LaFeAsO$_{1-x}$F$_x$ oxyarsenides as a function of temperature, the electrical resistivity of n-type Bi$_{88}$Sb$_{12}$ [14] was also shown.

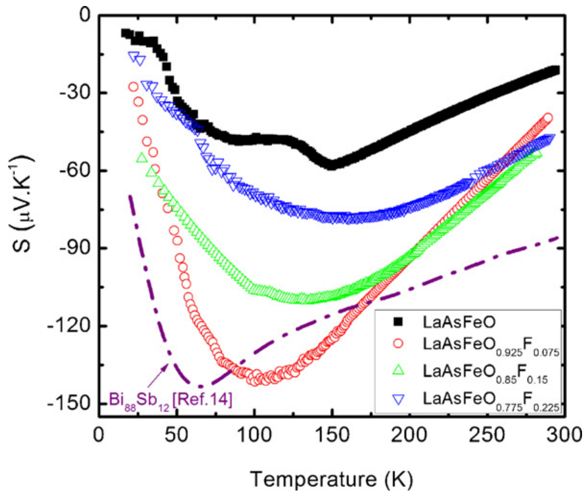

Fig. 3. Seebeck coefficient of LaFeAsO$_{1-x}$F$_x$ oxyarsenides as a function of temperature, Seebeck coefficient of n-type Bi$_{88}$Sb$_{12}$ [14] was also shown.

Fig. 3 shows the temperature dependence of Seebeck coefficient (S) for series LaFeAsO$_{1-x}$F$_x$ in the measuring temperature range from 20 K to 300 K. All the samples are n-type, which is consistent with an increase of the electrons concentration induced by the substitution of O by F. Undoped LaFeAsO sample exhibits a complex temperature dependence, and show an anomaly at about 150 K, which is similar to the *Ln*FeAsO (*Ln* = Sm and Nd) behavior reported previously [15]. This steep upturn just below 150 K is associated with the structural phase and/or SDW transition. This upturn in Seebeck coefficient disappears just after increasing F doped contents to $x = 0.075$, and the maximum values of Seebeck coefficient for series LaFeAsO$_{1-x}$F$_x$ samples decrease with increasing F doped contents and shift to high temperature. It can be seen that the maximum values of Seebeck coefficient significantly increase from −58 μV/K for LaFeAsO to −142 μV/K for LaFeAsO$_{0.925}$F$_{0.075}$, and decreases to −110 V/K for LaFeAsO$_{0.85}$F$_{0.15}$, and then reaches −78 μV/K as the F doped contents increase up to 0.225. As shown

Table 1
Maximum Seebeck coefficient (S_{max}) with corresponding temperature and superconductivity transition temperature (T_c) for some selected iron oxypnictides *Ln*FePnO.

Sample	S_{max} (μV/K)	T_c (K)	Ref.
$SmFe_{0.94}Ni_{0.06}AsO$	−68 at ∼110 K	10.0	[5]
$CeFe_{0.90}Co_{0.10}AsO$	−51 at ∼187 K	12.5	[8]
$SmFe_{0.90}Co_{0.10}AsO$	−80 at ∼150 K	17.2	[4]
$LaFeAsO_{0.90}F_{0.10}$	−100 at ∼125 K	26.8	[6]
$LaFeAsO_{0.85}F_{0.15}$	−110 at ∼105 K	28.7	This work
$Sm_{0.90}Th_{0.10}FeAsO_{0.85}F_{0.15}$	−120 at ∼80 K	55.0	[7]

in Fig. 3, it should be noted that $LaFeAsO_{0.925}F_{0.075}$ shows the maximum Seebeck coefficient value, which can be comparable to that of $Bi_{88}Sb_{12}$ thermoelectric materials [14]. However, the origin of enhancement of Seebeck coefficient in iron-oxypnictide superconductors is unclear and the variations of Seebeck coefficient cannot be explained easily due to the multiband nature of the electronic structure of these materials, whether this is related to strong electron correlations, magnetic fluctuations or SDW is an open issue. Wang et al. have suggested that enhancement of the Seebeck coefficient in $SmFe_{1-x}Co_xAsO$ and $LaFe_{1-x}Co_xAsO$ superconducting iron-oxypnictides could be somehow correlated to the onset of superconductivity [4]. Indeed, the enhancement of Seebeck coefficient is closely linked to superconductivity, which also has been found in some other superconducting iron-oxypnictides, such as $SmFe_{1-x}Ni_xAsO$ [5], $LaFe_{1-x}Zn_xAsO_{0.9}F_{0.1}$ [6], $Sm_{1-x}Th_xFeAsO_{1-y}F_y$ [7] and $CeFe_{1-x}Co_xAsO$ [8]. Maximum Seebeck coefficient with corresponding temperature and superconductivity transition temperature for some selected iron oxypnictides *Ln*FePnO are summarized in Table 1. As the emergence of superconductivity usually combines with suppressing the structural phase and/or SDW transition, it can be supposed that the present changes of Seebeck coefficient was determined by two competitive factors: enhance by suppressing the structural phase and/or SDW transition, and reduce by increasing carrier concentration. Hence, it can be explained that the significant enhancement of Seebeck coefficient in $LaFeAsO_{0.925}F_{0.075}$ appears just as suppressing SDW by F doping, after that, the Seebeck coefficient decreases with increasing carrier concentrations through further increasing F doped contents up to $x = 0.225$.

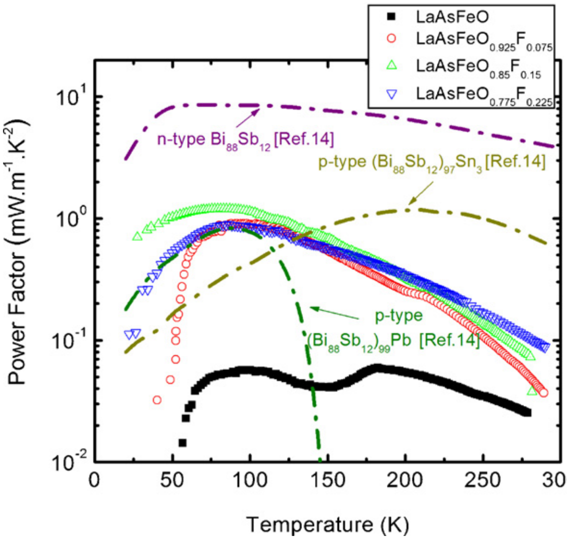

Fig. 4. Power factor of $LaFeAsO_{1-x}F_x$ oxyarsenides as a function of temperature, power factors of n-type $Bi_{88}Sb_{12}$, p-type $(Bi_{88}Sb_{12})_{99}Pb$ and p-type $(Bi_{88}Sb_{12})_{97}Sn_3$ [14] were also shown.

The power factors for $LaFeAsO_{1-x}F_x$ samples in the measuring temperature range from 20 K to 300 K has been calculated with the values of electrical resistivity and Seebeck coefficient, as shown in Fig. 4. The power factors for LaFeAsO oxypnictides was significantly improved by F doping, increases from 0.06 mW/mK^2 at 100 K for undoped LaFeAsO to 0.90 mW/mK^2 at 90 K for $LaFeAsO_{0.925}F_{0.075}$, and reaches the maximum value of 1.20 mW/mK^2 at 80 K for $LaFeAsO_{0.85}F_{0.15}$, and then decreases to 0.90 mW/mK^2 at 86 K for $LaFeAsO_{0.775}F_{0.225}$ as the F doped contents increase up to $x = 0.225$. For comparison, the power factors of n-type $Bi_{88}Sb_{12}$, p-type $(Bi_{88}Sb_{12})_{99}Pb$ and p-type $(Bi_{88}Sb_{12})_{97}Sn_3$ [14], the best low temperature thermoelectric materials, also were plotted in Fig. 4. The present maximum power factor of 1.20 mW/mK^2 for n-type $LaFeAsO_{0.85}F_{0.15}$ is in the same order, but 7 times lower than that of n-type $Bi_{88}Sb_{12}$. However, it should be emphasized that present samples are poorly densified polycrystalline, and that much lower electrical resistivity values can be expected for highly dense samples and single crystals. For instance, a resistivity of 2.5×10^{-4} Ω cm has been reported at 80 K in single crystals of $NdFeAsO_{0.7}F_{0.3}$ [16], and assuming a similar Seebeck coefficient, −142 μV/K, at 80 K for $LaFeAsO_{0.85}F_{0.15}$, this would correspond to a power factor of 3.6 mW/mK^2 which is about the same magnitude and nearly half of that in $Bi_{88}Sb_{12}$ [14]. It also should be noted that the present maximum power factor is higher than that of p-type $(Bi_{88}Sb_{12})_{99}Pb$ and p-type $(Bi_{88}Sb_{12})_{97}Sn_3$ [14]. It is well known that the performance of thermoelectric is evaluated by *ZT* value, high performance thermoelectric materials should have excellent electrical transport properties (S^2/ρ) and lower thermal conductivity (k). For LaFeAsO iron-oxypnictides, thermal conductivity is expected to be reduced by introducing lattice defects through F doing on O site. With considering the thermal conductivities of LaFeAsO [17] and $LaFeAsO_{0.89}F_{0.11}$ [18], the *ZT* value at 80 K for $LaFeAsO_{0.85}F_{0.15}$ has been calculated and reached about 0.015. Therefore, the present results indicate that $LaFeAsO_{1-x}F_x$ iron-oxypnictides are promising for thermoelectric cooling applications in the liquid nitrogen temperature range.

4. Conclusions

$LaFeAsO_{1-x}F_x$ compounds with different F doping contents have been successfully synthesized by a solid-state reaction method. Both electrical resistivity and Seebeck coefficient of undoped LaFeAsO show an anomaly related to a structural phase and/or spin-density-wave (SDW) transition at about 150 K. The electrical resistivity was reduced by increasing F doped contents, $LaFeAsO_{0.925}F_{0.075}$ sample showed the maximum Seebeck coefficient value of −142 μV/K just after suppressing the structural phase and/or spin-density-wave (SDW) transition by F doping. The maximum power factor of 1.20 mW/mK^2 at 80 K for $LaFeAsO_{0.85}F_{0.15}$ was obtained, which is about the same magnitude as that of n-type $Bi_{88}Sb_{12}$ that is the best low temperature thermoelectric material.

Acknowledgments

This work was supported by the *Triangle de la Physique* under project STP 2008-095T and *International Cooperation Department* of Université Paris-Sud XI.

References

[1] G.J. Snyder, E.S. Toberer, Nature Mater. 7 (2008) 105.
[2] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, H. Hosono, J. Am. Chem. Soc. 130 (2008) 3296.
[3] L. Pinsard-Gaudart, D. Berardan, J. Bobroff, N. Dragoe, Phys. Status Solidi (RRL) 2 (2008) 185.
[4] C. Wang, Y.K. Li, Z.W. Zhu, S. Jiang, X. Lin, Y.K. Luo, S. Chi, L.J. Li, Z. Ren, M. He, H. Chen, Y.T. Wang, Q. Tao, G.H. Cao, Z.A. Xu, Phys. Rev. B 79 (2009) 054521.

[5] Y.K. Li, X. Lin, T. Zhou, J.Q. Shen, Q. Tao, G.H. Cao, Z.A. Xu, J. Phys. Condens. Matter 21 (2009) 355702.

[6] Y.K. Li, X. Lin, Q. Tao, C. Wang, T. Zhou, L.J. Li, Q.B. Wang, M. He, G.H. Cao, Z.A. Xu, New J. Phys. 11 (2009) 053008.

[7] Y.K. Li, X. Lin, Q. Tao, H. Chen, C. Wang, L.J. Li, Y.K. Luo, M. He, Z.W. Zhu, G.H. Cao, Z.A. Xu, Chin. Phys. Lett. 26 (2009) 017402.

[8] L.D. Zhao, D. Berardan, L. Pinsard-Gaudart, C. Byl, N. Dragoe, J. Phys. Condens. Matter 22 (2010) 115701.

[9] J. Rodriguez-Carvajal, Phys. B 192 (1993) 55.

[10] J. Dong, H.J. Zhang, G. Xu, Z. Li, G. Li, W.Z. Hu, D. Wu, G.F. Chen, X. Dai, J.L. Luo, Z. Fang, N.L. Wang, Europhys. Lett. 83 (2008) 27006.

[11] C. de la Cruz, Q. Huang, J.W. Lynn, J.Y. Li, W.I.I. Ratcliff, J.L. Zarestky, H.A. Mook, G.F. Chen, J.L. Luo, N.L. Wang, P.C. Dai, Nature 453 (2008) 899.

[12] C. Wang, L.J. Li, S. Chi, Z.W. Zhu, Z. Ren, Y.K. Li, Y.T. Wang, X. Lin, Y.K. Luo, S. Jiang, X.F. Xu, G.H. Cao, Z.A. Xu, Europhys. Lett. 83 (2008) 67006.

[13] A.S. Sefat, A. Huq, M.A. McGuire, R.Y. Jin, B.C. Sales, D. Mandrus, L.M.D. Cranswick, P.W. Stephens, K.H. Stone, Phys. Rev. B 78 (2008) 104505.

[14] H. Noguchi, H. Kitagawa, T. Kiyabu, K. Hasezaki, Y. Noda, J. Phys. Chem. Solids 68 (2007) 91.

[15] M. Matusiak, T. Plackowski, Z. Bukowski, N.D. Zhigadlo, J. Karpinski, Phys. Rev. B 79 (2009) 212502.

[16] J. Jaroszynski, F. Hunte, L. Balicas, Y.-J. Jo, I. Raicevic, A. Gurevich, D.C. Larbalestier, F.F. Balakirev, L. Fang, P. Cheng, Y. Jia, H.H. Wen, Phys. Rev. B 78 (2008) 174523.

[17] M.A. McGuire, A.D. Christianson, A.S. Sefat, B.C. Sales, M.D. Lumsden, R.Y. Jin, E.A. Payzant, D. Mandrus, Y.B. Luan, V. Keppens, V. Varadarajan, J.W. Brill, R.P. Hermann, M.T. Sougrati, F. Grandjean, G.J. Long, Phys. Rev. B 78 (2008) 094517.

[18] A.S. Sefat, M.A. McGuire, B.C. Sales, R.Y. Jin, J.Y. Howe, D. Mandrus, Phys. Rev. B 77 (2008) 174503.