A comparative study on the thermoelectric effect of parent oxypnictides LaTAsO (T = Fe, Ni)

FAST TRACK COMMUNICATION

A comparative study on the thermoelectric effect of parent oxypnictides LaTAsO (T = Fe, Ni)

Qian Tao[1], Zengwei Zhu[1], Xiao Lin[1], Guanghan Cao[1],
Zhu-an Xu[1,3], Genfu Chen[2], Jianlin Luo[2] and Nanlin Wang[2]

[1] Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China
[2] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics,
Chinese Academy of Sciences, Beijing 100080, People's Republic of China

E-mail: zhuan@zju.edu.cn

Abstract
The thermopower and Nernst effect were investigated for undoped parent compounds LaFeAsO and LaNiAsO. Both the thermopower and Nernst signal in iron-based LaFeAsO are significantly larger than those in nickel-based LaNiAsO. Furthermore, abrupt changes in both the thermopower and Nernst effect are observed below the structural phase transition temperature and spin-density wave (SDW) type antiferromagnetic (AFM) order temperature in Fe-based LaFeAsO. On the other hand, the Nernst effect is very small in the Ni-based LaNiAsO and it is weakly temperature-dependent, reminiscent of the case in normal metals. We suggest that the effect of SDW order on the spin scattering rate should play an important role in the anomalous temperature dependence of the Hall effect and Nernst effect in LaFeAsO. The contrasting behaviour between the LaFeAsO and LaNiAsO systems implies that the LaFeAsO system is fundamentally different from the LaNiAsO system and this may provide clues to the mechanism of high T_c superconductivity in Fe-based systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The recent discovery of superconductivity in layered 1111 phase quaternary compounds RTPnO (R = lanthinides, T = Fe and Ni, Pn = P and As) has attracted tremendous attention to this class of materials [1–8]. Besides these 1111 phase oxypnictides, superconductivity was subsequently discovered in other iron(nickel)-based layered compounds with similar Fe(Ni)As layers [9–12]. In all the FeAs-based parent compounds, there is a structural phase transition in the temperature range 100–200 K, and a spin-density wave (SDW) type antiferromagnetic (AFM) ordering associated with Fe ions accompanies the structural transition [13–15]. Various chemical doping approaches, or the application of high pressure, can

suppress the structural transition and AFM order, and high-T_c superconductivity consequently appears. For example, in the FeAs-based La-1111 system, superconductivity has been achieved by chemical doping at four different crystallographic sites [2, 6, 7, 16–18]. Meanwhile, low-T_c superconductivity has been observed in FeP-based [1] and NiAs(P)-based [8, 19] compounds with similar layered structure, but there is neither a structural transition nor AFM ordering associated with Fe(Ni) ions in these compounds. Furthermore, many reports have found that both normal state properties and the superconductivity of the NiAs-based systems are most probably of the conventional type [8, 19]. This result suggests that there could be a close relationship between the structural transition/AFM order and high-T_c superconductivity. Moreover, the origin of the AFM order in the parent FeAs-based pnictides is still an open

---

[3] Author to whom any correspondence should be addressed.

1

issue theoretically. Regardless of the origin of the AFM ordering, several theories have suggested that the superconductivity is tied to the magnetism in the FeAs-based materials [20–23]. All these results imply that the mechanism of superconductivity in FeAs-based systems could be fundamentally different to NiAs-based systems. Systematic investigation of the physical properties of these parent pnictides could shed light on the mechanisms of superconductivity.

Thermoelectric effects are very sensitive to subtle changes in electronic structure, and can provide information on the ground state and low energy excitations. In particular, the transverse magneto-thermoelectric effect, i.e., the Nernst effect, which is defined as the appearance of a transverse electric field E_y in response to a temperature gradient $\nabla T \parallel x$ in the presence of a perpendicular magnetic field $H \parallel z$ and under open circuit conditions, has become a powerful probe in studying exotic superconductors, such as high-T_c cuprates [24], charge-density wave (CDW) superconductor NbSe$_2$ [25], heavy fermion superconductors [26], and p-wave superconductor Sr$_2$RuO$_4$ [27] etc. The first report on the Nernst effect in a F-doped LaFeAsO superconductor discovered that the vortex liquid regime below T_c is quite large [28], consistent with the simulation result [29], and there is an enhanced anomalous Nernst signal just above T_c.

Here we report the systematic investigation on the thermopower and Nernst effect of FeAs-based and NiAs-based parent oxypnictides. Both the thermopower and Nernst coefficient of the undoped LaFeAsO system are significantly large compared to usual metals, and the structural/AFM transition causes anomalous changes in the thermoelectric properties. However, the thermopower and Nernst effect of the NiAs-based LaNiAsO system are most probably of the conventional type, implying usual Fermi liquid behaviour. The fundamental difference in the thermoelectric properties of the two systems suggests that there is a close relationship between high-T_c superconductivity and the anomalous thermoelectric properties in FeAs-based systems.

2. Experimental details

The polycrystalline samples of LaFeAsO and LaNiAsO were prepared by a solid state reaction using LaAs, Fe$_2$O$_3$/NiO, Fe/Ni and LaF$_3$ as starting materials. The sample preparation details can be found in a previous report [8]. The powder x-ray diffraction patterns indicate that the resultant is single phase and all the diffraction peaks can be well indexed based on the tetragonal ZrCuSiAs-type structure with the space group $P4/nmm$.

The resistivity was measured by the usual four-probe method. The Hall effect was measured by scanning the magnetic field at fixed temperatures. The thermoelectric properties were measured by a steady-state technique. The temperature gradient used for the thermoelectric measurements, measured by a pair of differential type E thermocouples, was around 0.5 K mm^{-1}. All the measurements were performed in a Quantum Design PPMS-9 system. The Nernst signal e_y is defined as $e_y \equiv \frac{E_y}{|\nabla T|}$. The Nernst signal was measured at positive and negative field
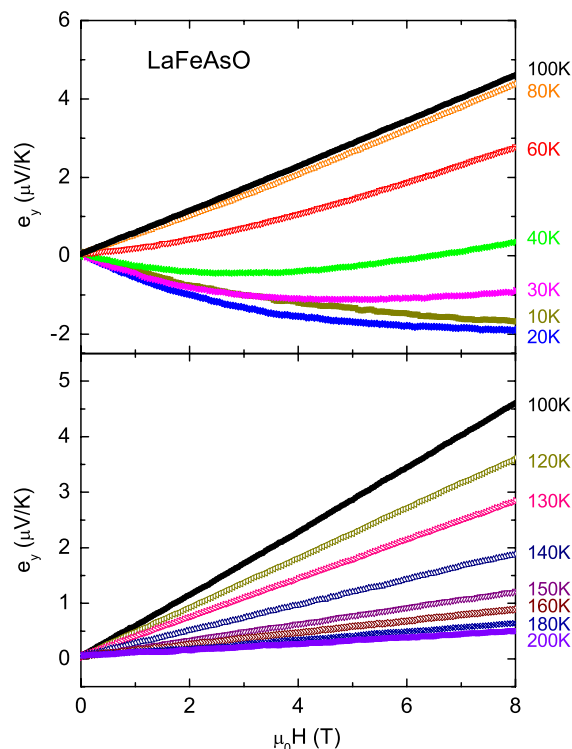

Figure 1. Magnetic field dependence of the Nernst signal (e_y) at different temperatures for LaFeAsO.

polarities, and the difference of the two polarities was taken to remove any thermopower contributions. The Nernst coefficient ν_N is equal to e_y/B. At very low temperatures, e_y is not strictly linear with magnetic field H, the Nernst coefficient is then taken as the initial slope of the e_y versus $\mu_0 H$ curves.

3. Results and discussion

3.1. Thermoelectric effects of LaFeAsO

Traces of the Nernst signal as a function of magnetic field up to $\mu_0 H$ of 8 T for the parent oxypnictide LaFeAsO are displayed in figure 1 at various temperatures. At high temperatures (see the lower panel of figure 1), the Nernst signal (e_y) is positive and changes linearly with magnetic field. The Nernst signal reaches a maximum around 100 K. Below 100 K, the Nernst signal decreases, and becomes a little nonlinear with magnetic field as $T < 80$ K. Between 40 and 60 K, the Nernst signal changes from positive to negative. Such a sign change might not necessarily suggest a change in the charge carrier type. In multi-band systems, the contributions of different bands to the Nernst signal could have different signs.

The temperature dependence of the Nernst coefficient, $\nu_N(T)$, together with its thermopower, $S(T)$, is shown in figure 2. The temperature dependence of thermopower is consistent with previous reports [30–32], which exhibits a pronounced hump as the system undergoes the structural phase transition/AFM ordering at a T^* of about 160 K, where T^* is the structural phase transition temperature and can be determined by the resistivity measurements. The Nernst
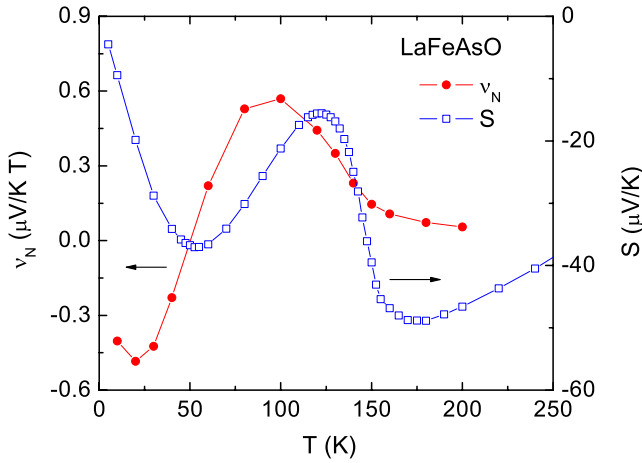
Figure 2. Temperature dependence of the Nernst coefficient for LaFeAsO. The thermopower measured under zero magnetic field is also shown.

coefficient is defined as the initial slope of the e_y–H curves for $T < 80$ K. The Nernst coefficient is positive and shows a weak temperature dependence when $T > T^*$ of about 160 K. However ν_N starts to increase below a T^* of 160 K, reaches a maximum around 100 K, and then decreases with decreasing temperatures. With further cooling, it changes sign around 50 K, and then reaches a minimum (valley) around 20 K before it finally goes to zero. Compared to the usual metals and the normal state of high-T_c cuprates, $\nu_N(T)$ is much larger.

In order to get more insight on the thermoelectric effect, the ratio of ν_N/S is calculated and plotted in the upper panel of figure 3. There is a very clear sharp drop in ν_N/S as the system becomes AFM ordered below T^*. But the ratio increases monotonously with further cooling. By measuring the Hall effect and thermopower simultaneously, the off-diagonal thermoelectric (Peltier conductivity) term can be separated from the Nernst signal and then both the Hall angle $\tan\theta$ (defined as ρ_{xy}/ρ) and 'thermal' Hall angle $\tan\theta_{th}$ (defined as α_{xy}/α) can be obtained. The temperature dependence of the Hall coefficient (R_H) measured under a magnetic field ($\mu_0 H$) of 8 T is also shown in the upper panel of figure 3. R_H is negative, suggesting that the dominant charge carrier is electron-like, consistent with previous reports [33–35]. The R_H is about -4.8×10^{-9} m^3 C^{-1} at $T = 300$ K, corresponding to a Hall number ($n_H = 1/(eR_H)$) of about 0.18 electrons per unit cell, which could be an upper limit for the electron concentration n_e because LaFeAsO is a nearly compensated metal according to the band calculations [36]. For comparison, the more metallic BaFe$_2$As$_2$ has a Hall number of about 0.56 electrons per unit cell at room temperature according to the Hall effect measurements, but band calculations predict a Hall number of 0.15 electrons per unit cell [37].

The normal state Nernst signal is comprised of two terms, namely

$$e_y = \rho\alpha_{xy} - S\tan\theta = S(\tan\theta_{th} - \tan\theta), \quad (1)$$

where α_{xy} is the off-diagonal Peltier coefficient, $S = \frac{\alpha}{\sigma}$ the thermopower (σ the diagonal conductivity and α the diagonal
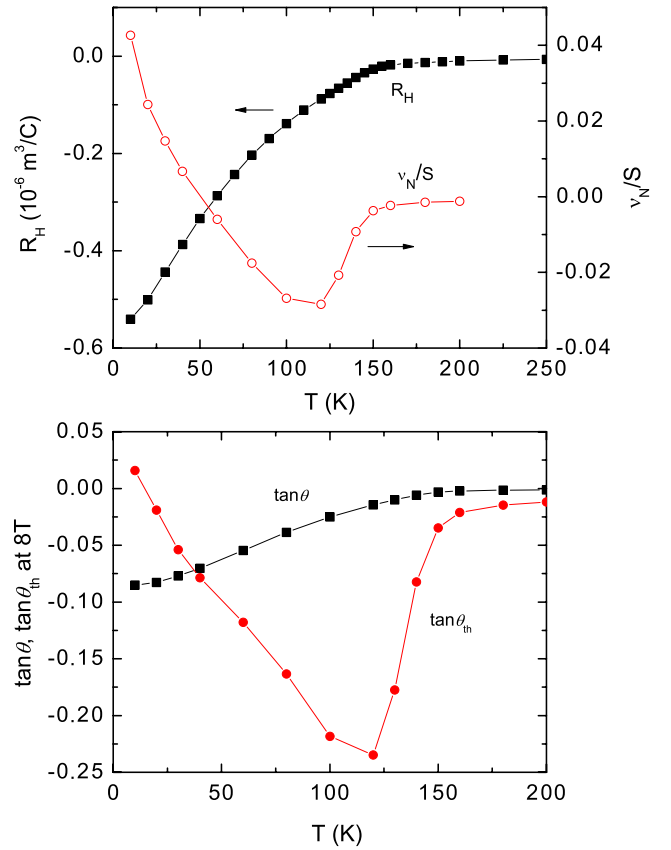

Figure 3. Upper panel: the Hall coefficient (R_H) and the ratio of ν_N/S versus temperature for LaFeAsO. The Hall effect was measured under a magnetic field ($\mu_0 H$) of 8 T. Lower panel: temperature dependence of the Hall angle $\tan\theta$ and 'thermal' Hall angle $\tan\theta_{th}$ at a $\mu_0 H$ of 8 T for LaFeAsO. See text for more details.

Peltier coefficient), ρ the resistivity, $\tan\theta$ the Hall angle, and $\tan\theta_{th}$ the 'thermal' Hall angle. For usual simple metals, the two terms related to the Hall angle and 'thermal' Hall angle in equation (1) cancel each other; this is so-called 'Sondheimer cancellation' [38, 39]. It is known that the Hall angle, rather than the Hall coefficient, is directly related to the scattering rate of the quasiparticle scattering. The Hall angle can be calculated from the Hall coefficient, i.e., $\tan\theta = \rho_{xy}/\rho$, and then the 'thermal' Hall angle can be obtained from the Nernst signal by using equation (1). The Hall angle and 'thermal' Hall angle obtained are plotted in the lower panel of figure 3 as a function of temperature. The two angles exhibit very different temperature dependence, especially the decrease in the 'thermal' Hall angle, which is much more significant below T^*. It becomes clear that the Sondheimer cancellation of the Nernst signal no longer holds for LaFeAsO because of the different temperature dependence of the two angles below T^*. Even above T^*, the Nernst coefficient is also larger than that of usual metals. The enhanced Nernst signal above T^* could result from the multi-band effect. The presence of two types of charge carriers in multi-band systems, such as NbSe$_2$ [25], could invalidate the Sondheimer cancellation, resulting in a large Nernst signal. However it is hard to understand the anomalous temperature dependence of ν_N below T^*, even in the frame of multi-band effect. There might be significant
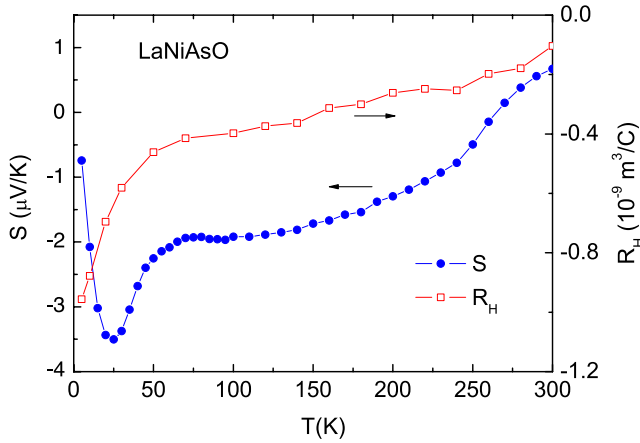
Figure 4. Temperature dependence of the thermopower and Hall coefficient for LaNiAsO. The Hall effect was measured under a magnetic field ($\mu_0 H$) of 5 T.

Figure 5. Magnetic field dependence of the Nernst signal (e_y) at selected temperatures for LaNiAsO.

changes in the scattering mechanism below T^*, and these changes seem to have a more pronounced influence on the thermal channel. We propose that the SDW order or SDW fluctuations could affect the spin-dependent scattering process and thus cause significant changes in the scattering rates, which could be band-dependent. Subtle changes in the scattering mechanism could cause the anomalous Nernst effect, as observed in the p-wave superconductor Sr_2RuO_4 [27].

The first-principles band calculations have proposed that the nesting between the electron-type Fermi surface (FS) and hole-type FS could account for the AFM transition in the parent compounds, such as LaFeAsO, and that the superconductive pairing might be mediated by spin fluctuations [13, 20, 36]. Moreover, the studies of angle-resolved photoemission spectroscopy (ARPES) discovered that the coexistence of hole and electron pockets connected via the AFM wavevector is essential to high-T_c superconductivity [40, 41]. The AFM order and structural phase transition in the parent compounds causes significant changes in the electronic structure. Based on our measurements of resistivity and the Hall effect, the charge carrier concentration in LaFeAsO estimated by the Hall number decreases by a factor of about 100 and the scattering rate (in inverse proportion to the mobility) also decreases by a factor of about 160 as the temperature decreases from 300 to 10 K. For the parent compound $BaFe_2As_2$, similar results were reported [37, 42]. Such changes in the charge carrier concentration and scattering rates in the parent compounds $BaFe_2As_2$, $SrFe_2As_2$, and $EuFe_2As_2$ were also reported by optical spectroscopy measurements [43, 44]. All the results suggest that the charge carrier transport is dominated by the AFM fluctuations in the parent compounds. When the system undergoes the AFM order below about 160 K, the charge carrier concentration deceases sharply due to the SDW gapping on FSs, but the scattering rates decrease even more drastically due to the AFM order, which suppresses the spin fluctuations. It can be seen from figure 3, the AFM order may have a more pronounced influence on the thermal channel. Thus our results imply that the anomalous changes in the thermopower and Nernst coefficient in LaFeAsO should have a close relation
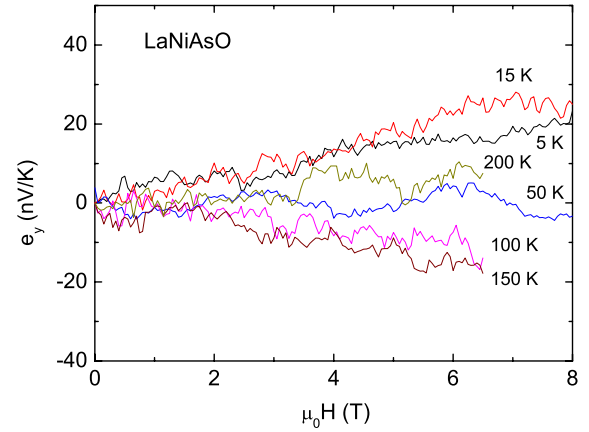
with the inter-band scattering between electron-type and hole-type bands.

3.2. Thermoelectric effects of LaNiAsO

The thermopower and Hall coefficient (measured under $\mu_0 H$ of 5 T) of LaNiAsO are plotted as a function of temperature in figure 4. The negative R_H implies that the charge carriers are dominantly electron type, the same as in LaFeAsO. The absolute value of R_H for LaNiAsO is more than 1 order of magnitude smaller than that of LaFeAsO, possibly indicating that the LaNiAsO system has a relatively higher carrier density. The Hall number n_H at $T = 300$ K is about 8.3 electrons per unit cell, about 50 times larger compared to LaFeAsO. Since $Ni^{2+}3d^8$ contributes two more electrons than the Fe ion does, the Fermi energy shifts up in LaNiAsO, and the hole bands tend to be fully filled. As a result, predicted by band calculations [36], the electron bands dominate the conductivity in LaNiAsO [8]. The much smaller thermopower also suggests that LaNiAsO is a good metal with a high density of charge carriers compared to LaFeAsO. The small hollow in S at low temperature could be caused by the phonon drag effect. It is interesting that R_H also exhibits a sharp decrease below 50 K. Such a change in R_H at low temperature is not yet well understood.

Traces of the Nernst signal as a function of magnetic field for LaNiAsO are displayed in figure 5 at several selected temperatures. The Nernst signal (e_y) is very small, comparable to the noise level (the noise voltage is about 10 nV in our measurement system). This Nernst signal is as small as in usual metals. e_y at $\mu_0 H$ of 6 T is only in the range of ± 30 nV K^{-1}, almost two orders of magnitude smaller than that of LaFeAsO. The Nernst coefficient is obtained by fitting the e_y versus H curves with a linear function, and it is plotted in figure 6. The Hall angle $\tan\theta$ and the term $S\tan\theta$ are also plotted in figure 6 for comparison. It can seen that the Nernst coefficient is comparable to the term $S\tan\theta$, implying that the Sondheimer cancellation is partially held and the system could be dominated by only one type charge carrier (electron). Please note that the temperature dependence of $\tan\theta$ is very weak and
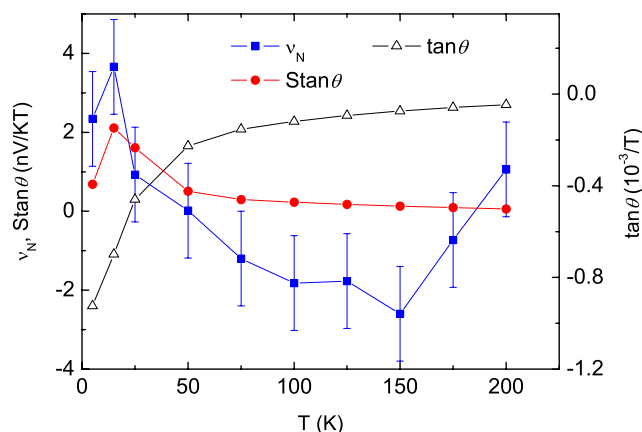
Figure 6. Nernst coefficient versus temperature for LaNiAsO. The Hall angle $\tan\theta$ and the term $S\tan\theta$ are also plotted, where the Hall angle $\tan\theta$ is normalized to a $\mu_0 H$ of 1 T.

its magnitude is much smaller than that of LaFeAsO, especially at low temperatures.

This result for the Nernst effect suggests that LaNiAsO is like a usual metal and only one type (electron-type) of charge carrier dominates. Xu *et al* [36] compared the band structures of LaFeAsO and LaNiAsO by first-principles calculations. It was found that the electron FS cylinders around the M point becomes larger for LaNiAsO, and the hole-type FS cylinders around the Γ point disappear. Thus the nesting between hole-type FSs and electron-type FSs proposed in LaFeAsO no longer holds in LaNiAsO. Recall that the multi-band effect could account for the enhanced Nernst signals in both parent and F-doped LaFeAsO, which have relatively high superconducting transition temperatures, the inter-band scattering should indeed play an important role in the occurrence of high T_c. On the other hand, our result suggests that the LaNiAsO system lacks such an inter-band scattering mechanism, and thus it has a low T_c. The relationship between high-T_c superconductivity and the inter-band scattering is worth further experimental investigations.

4. Conclusions

In summary, we report the thermopower and Nernst effect of FeAs-based and NiAs-based parent oxypnictides. For the LaFeAsO system, it is found that both the thermopower and Nernst coefficient are significantly large compared to usual metals and the structural/AFM transition associated with Fe ions causes significant enhancements in the thermoelectric coefficients. We propose that unique strong inter-band scattering as well as electron correlation in FeAs-based systems may account for these anomalies in the thermoelectric properties. Meanwhile, the thermopower and Nernst effect of the NiAs-based LaNiAsO system are of conventional type, implying usual Fermi liquid behaviour. The fundamental difference in the thermoelectric properties of the two systems suggests that there is a close relationship between the high-T_c superconductivity and the anomalous thermoelectric properties in FeAs-based pnictides.

References

[1] Kamihara Y, Hiramatsu H, Hirano M, Kawamura R, Yanagi H, Kamiya T and Hosono H 2006 *J. Am. Chem. Soc.* **128** 10012
[2] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[3] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 *Nature* **453** 761
[4] Chen G F, Li Z, Wu D, Li G, Hu W, Dong J, Zheng P, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **100** 247002
[5] Ren Z *et al* 2008 *Europhys. Lett.* **83** 17002
[6] Wen H H, Mu G, Fang L, Yang H and Zhu X 2008 *Europhys. Lett.* **82** 17009
[7] Wang C *et al* 2008 *Europhys. Lett.* **83** 67006
[8] Li Z *et al* 2008 *Phys. Rev.* B **78** 060504(R)
[9] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
[10] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 *Solid State Commun.* **148** 538
[11] Hsu F C *et al* 2008 arXiv:0807.2369
[12] Ogino H, Matsumura Y, Katsura Y, Ushiyama K, Horii S, Kishio K and Shimoyama J 2009 *Supercond. Sci. Technol.* **22** 075008
[13] Dong J *et al* 2008 *Europhys. Lett.* **83** 27006
[14] de la Cruz C *et al* 2008 *Nature* **453** 899
[15] Huang Q, Qiu Y, Bao W, Lynn J W, Green M A, Chen Y, Wu T, Wu G and Chen X H 2008 *Phys. Rev. Lett.* **101** 257003
[16] Sefat A S, Huq A, McGuire M A, Jin R, Sales B C and Mandrus D 2008 *Phys. Rev.* B **78** 104505
[17] Wang C *et al* 2009 *Phys. Rev.* B **79** 054521
[18] Wang C *et al* 2009 *Europhys. Lett.* **86** 47002
[19] Watanabe T, Yanagi H, Kamihara Y, Kamiya T, Hirano M and Hosono H 2008 *J. Solid State Chem.* **181** 2117
[20] Mazin I I, Singh D J, Johannes M D and Du M H 2008 *Phys. Rev. Lett.* **101** 057003
[21] Yildirim T 2008 *Phys. Rev. Lett.* **101** 057010
[22] Ma F, Lu Z-Y and Xiang T 2008 *Phys. Rev.* B **78** 224517
[23] Seo K, Bernevig B A and Hu J P 2008 *Phys. Rev. Lett.* **101** 206404
[24] Xu Z A, Ong N P, Wang Y, Kakeshita T and Uchida S 2000 *Nature* **406** 486
[25] Bel R and Behnia K 2003 *Phys. Rev. Lett.* **91** 066602
[26] Bel R, Behnia K, Nakajima Y, Izawa K, Matsuda Y, Shishido H, Settai R and Onuki Y 2004 *Phys. Rev. Lett.* **92** 217002
[27] Xu X F, Xu Z A, Liu T J, Fobes D, Mao Z Q, Luo J L and Liu Y 2008 *Phys. Rev. Lett.* **101** 057002
[28] Zhu Z W, Xu Z A, Lin X, Cao G H, Feng C M, Chen G F, Li Z, Luo J L and Wang N L 2008 *New J. Phys.* **10** 063021
[29] Lv J P and Chen Q H 2008 *Phys. Rev.* B **78** 144507
[30] McGuire M A *et al* 2008 *Phys. Rev.* B **78** 094517
[31] Li L *et al* 2008 *Phys. Rev.* B **78** 132506
[32] Li Y *et al* 2009 *New J. Phys.* **11** 053008
[33] Chen G F *et al* 2008 *Phys. Rev. Lett.* **101** 057007
[34] Yang H, Zhu X, Fang L, Mu G and Wen H H 2008 *Supercond. Sci. Technol.* **21** 105001

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

[36] Xu G, Ming W, Yao Y, Dai X, Zhang S C and Fang Z 2008 *Europhys. Lett.* **82** 67002

[37] Fang L *et al* 2009 *Phys. Rev.* B **80** 140508(R)

[38] Sondheimer E H 1948 *Proc. R. Soc.* A **193** 484

[39] Wang Y, Xu Z A, Kakeshita T, Uchida S, Ono S, Ando Y and Ong N P 2001 *Phys. Rev.* B **64** 224519

[40] Sekiba Y *et al* 2009 *New J. Phys.* **11** 025020

[41] Terashima K *et al* 2009 *Proc. Natl Acad. Sci.* **106** 7330

[42] Rullier-Albenque F, Colson D, Forget A and Alloul H 2009 *Phys. Rev. Lett.* **103** 057001

[43] Hu W Z, Dong J, Li G, Li Z, Zheng P, Chen G F, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **101** 257005

[44] Wu D *et al* 2009 *Phys. Rev.* B **79** 155103