J Supercond Nov Magn (2009) 22: 667–670
DOI 10.1007/s10948-009-0463-z

ORIGINAL PAPER

Pressure Effect on Superconductivity and Magnetism in α-FeSe$_x$

**L. Li · Z.R. Yang · M. Ge · L. Pi · J.T. Xu · B.S. Wang ·
Y.P. Sun · Y.H. Zhang**

Received: 11 March 2009 / Accepted: 30 March 2009 / Published online: 9 April 2009

Abstract In this paper, the pressure effect on superconductivity and magnetism has been investigated in FeSe$_x$ ($x = 0.80, 0.88$). The magnetization curves display anomaly at $T_{s1} \sim 106$ K and $T_{s2} \sim 78$ K except for the superconducting diamagnetic transition around $T_c \sim 8$ K. The magnetic anomaly at T_{s1} and T_{s2} can be related to a ferromagnetic and an antiferromagnetic phase transition, respectively, as revealed by specific heat measurements. The application of pressure not only raises T_c, but also increases both T_{s1} and T_{s2}.

Keywords Fe-based superconductors · Superconductivity · Pressure effect

PACS 74.62.Fj · 74.70.-b

The discovery of superconductivity in doped LaFeAsO has generated much attention in layered FeAs systems [1–5]. The parent LaFeAsO material shows a structural transition from tetragonal to orthorhombic crystal symmetry at 150 K, followed by the formation of spin-density-wave (SDW) at a slightly lower temperature around 140 K [3]. Doping with fluorine suppresses the SDW and leads the onset of superconductivity. Therefore, this system is close to magnetic instability, and the superconductivity in the doped systems seems to be of unconventional nature [4, 5].

Very recently, Hsu et al. reported the observation of superconductivity with critical temperature T_c around 8 K in another Fe-based system, the PbO-type α-FeSe compound [6]. Subsequently, T_c has been raised to 27 K with the application of high pressure [7]. Compared with the layered FeAs systems, α-FeSe not only has the same planar sublattices but also displays structure and magnetism instability [8–10]. Density functional study showed that α-FeSe has the SDW ground state [11]. First principles studies by Lee et al. provided evidence that the ground state for stoichiometric α-FeSe is nonmagnetic and the magnetism is driven by anion vacancy [12]. Upon cooling, a structural transition from tetragonal to triclinic symmetry around 105 K accompanied by magnetic anomaly was reported by Hsu et al. [6]. However, Margadonna et al. observed a tetragonal-orthorhombic structural transition at 75 K [13]. Although these results are inconsistent, α-FeSe seems to be a superconductor with strong magnetic character, and the superconductivity might correlate with the structural transition. Therefore, a delicate modulation of the structural transition by pressure and magnetic field will be helpful for understanding the superconductivity in this system.

In the paper, the superconductivity in PbO-type α-FeSe$_x$ has been examined with two nominal compositions ($x = 0.80, 0.88$). Especially, we investigated the pressure effect on the superconductivity and magnetism. Both samples show superconductivity with $T_c \sim 8$ K. With the decrease of temperature at ambient pressure, the field-cooling magnetization displays a sharp upturn around $T_{s1} \sim 106$ K and an abrupt decrease at $T_{s2} \sim 78$ K, in consistent with the results of Hsu et al. and Fang et al. [6, 8]. Magnetic field dependent specific heat measured for $x = 0.88$ shows that T_{s1} and T_{s2} can be related to a ferromagnetic and an anti-ferromagnetic

L. Li · M. Ge · L. Pi · J.T. Xu · Y.H. Zhang
National High Magnetic Field Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China

Z.R. Yang (✉) · B.S. Wang · Y.P. Sun
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
e-mail: zryang@issp.ac.cn

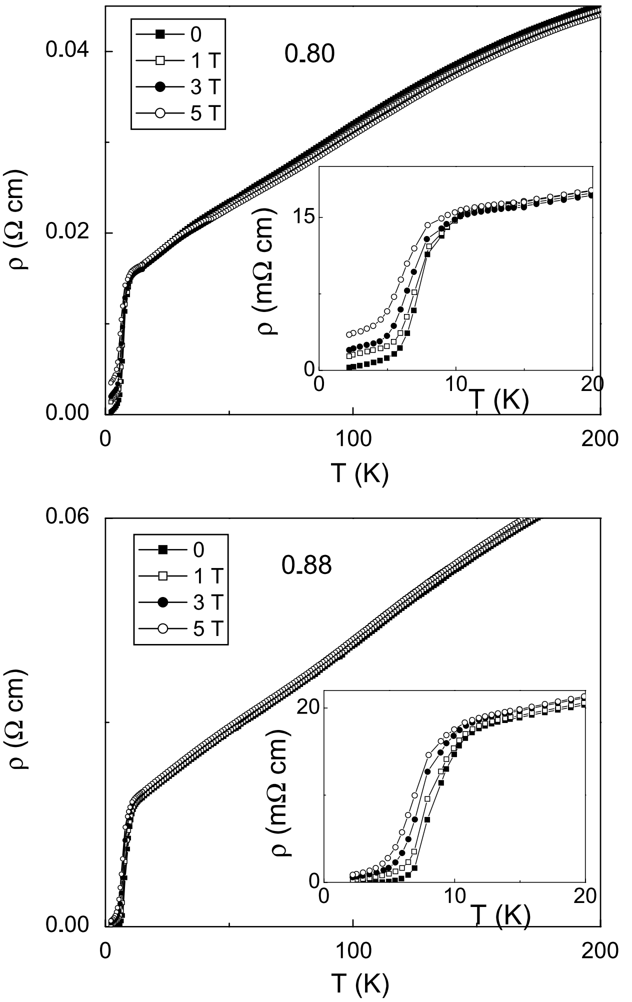

Fig. 1 Temperature dependence of resistivity for $FeSe_x$ ($x = 0.80, 0.88$) at different fields. *Insets* show enlarged views of the superconducting transition for both samples

phase transition, respectively. The applied pressure not only raises T_c, both also increases both T_{s1} and T_{s2}, contrary to the conjecture of Margadonna et al. [13].

The polycrystalline samples with nominal compositions $FeSe_x$ ($x = 0.80, 0.88$) were prepared by standard solid-state synthesis method. High-purity powders of iron (99.9%) and selenium (99.9%) were mixed uniformly in a 2 g batch, then sealed into evacuated quartz tubes and heat treated at 700°C for 24 hours. The initially sintered samples were ground and pressed into round-shaped pellets (10 mm diameter, 2 mm thick). The pellets were re-sealed in evacuated quartz tubes and sintered at 700°C for another 24 hours.

Structure and phase purity of the samples were examined by an X-ray power diffraction (XRD) method, with Cu K_α radiation at room temperature. In agreement with the results of Hsu et al. [6], the prepared samples are composed of primarily PbO-type α-FeSe ($P4/nmm$) and tiny amount of impurity phases, the impurity was identified to be element Se and β-FeSe. The resistivity was measured using a standard four-probe method from 2.5 to 300 K in a Quantum Design Physical Properties Measurement System (PPMS). The specific heat was measured with thermal relaxation method in PPMS. Temperature dependence of magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer. The application of pressure was performed in an Easylab Mcell 10 Pressure cell.

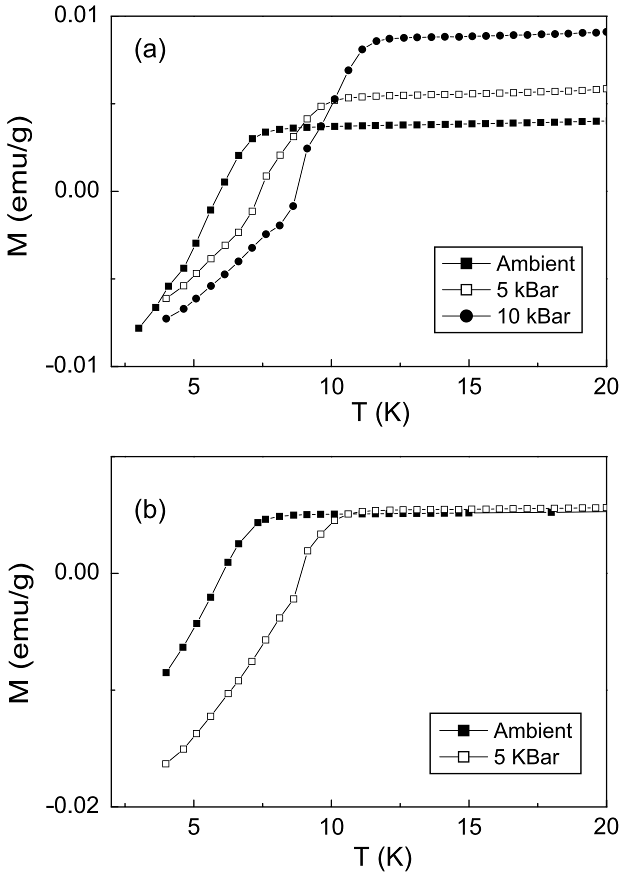

Fig. 2 Zero field cooling (ZFC) magnetization under different pressures around the superconducting transition temperature for (**a**) $x = 0.80$ and (**b**) $x = 0.88$

Figure 1 displays the temperature dependence of resistivity ρ in the field range from 0 to 5 T. Upon cooling, both samples display metallic behavior before the onset of superconductivity around $T_c^{\mathrm{Res}} \sim 10$ K. With increasing magnetic field, the critical temperature decreases monotonously. By defining the critical temperature T_c with criterion of $\rho_{\mathrm{cri}} = 50\%\rho_n$, the upper critical field deduced at 0 K $H_{c2}(0)$ for $x = 0.88$ is about 27 T, similar to the result of Mizuguchi et al. [7].

The temperature dependence of magnetization (M) was measured at 10 Oe in both field cooling (FC) and zero field cooling (ZFC) sequence for $x = 0.80$ and 0.88. Both samples at ambient pressure show clear superconducting diamagnetic response below the onset temperature T_c^{mag} around 8 K, see Fig. 2. With increasing pressure, T_c^{mag} in-

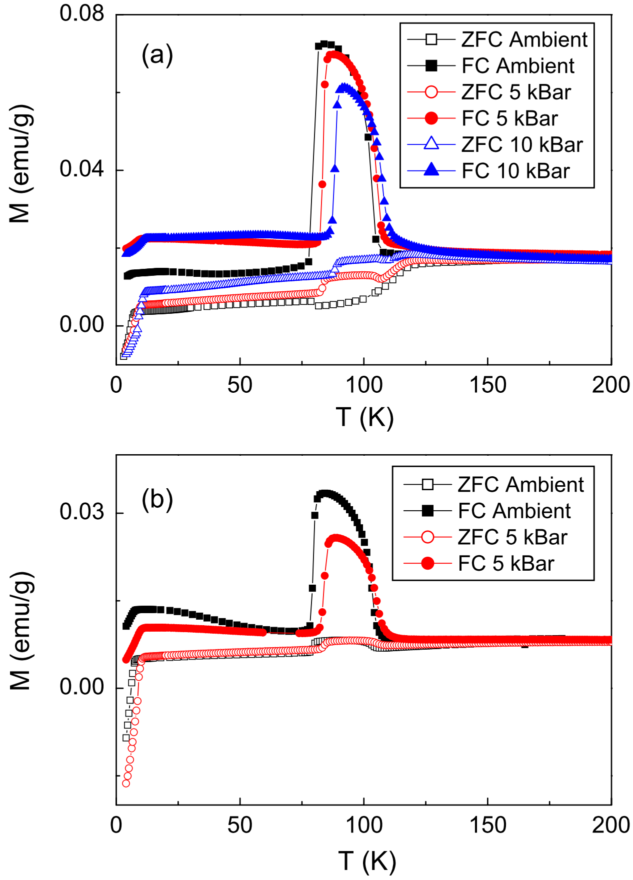

Fig. 3 Temperature dependence of magnetization under different pressures for (**a**) $x = 0.80$ and (**b**) $x = 0.88$. The magnetization has been measured at 10 Oe in both field cooling (FC) and zero-field cooling (ZFC) sequence

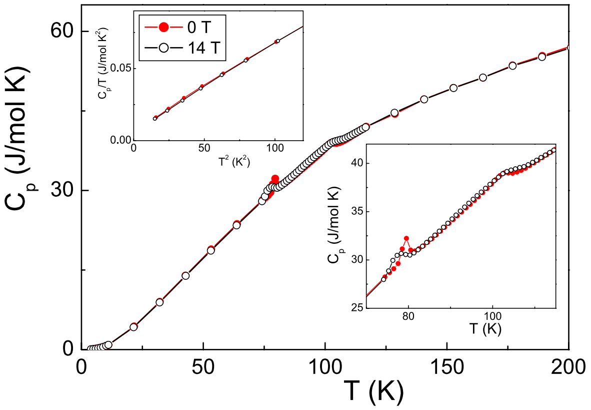

Fig. 4 Temperature dependence of specific heat for $x = 0.88$ sample under magnetic field of 0 and 14 T. *Inset* (**a**) displays C_p/T as a function of T^2 around T_c. *Inset* (**b**) shows enlarged view of $C_p(T)$ around T_{s1} and T_{s2}

creases. The estimated pressure coefficient $\mathrm{d}T_c/\mathrm{d}P$ is about 0.4 K/kbar, similar to the value Mizuguchi et al. derived from the pressure effect on zero resistivity temperature, but less than the value of pressure effect on the onset resistive transition [7]. Compared with the results of Mizuguchi et al., the lower pressure coefficient might be due to different measuring methods. Looking at Fig. 1 and Fig. 2, the onset critical temperature of the resistive transition T_c^{Res} is larger than that of the diamagnetic transition T_c^{mag}.

Figure 3 displays $M(T)$ curves at different pressures in a broad temperature range from 4.5 K to 200 K. At ambient pressure, both ZFC and FC magnetization shows anomaly at $T_{s1} \sim 106$ K and $T_{s2} \sim 78$ K, respectively. Upon cooling, the FC magnetization first increases abruptly at T_{s1} then displays a sharp decrease and restores to its high temperature value at T_{s2}, signaling two magnetic transitions. Around the first transition temperature T_{s1}, Hsu et al. found a tetragonal-triclinic structure transition [6]. Near the second transition temperature T_{s2}, Margadonna et al. reported a tetragonal-orthorhombic structural transition, independently [13]. Therefore, the magnetic anomalies should be intrinsic behavior of the superconducting α-FeSe with tetragonal crystal symmetry, which is related to the structural and magnetic instabilities.

In order to understand the nature of magnetic anomalies, we further performed specific heat measurement for $x = 0.88$ sample under magnetic field of 0 and 14 T, respectively. As shown in Fig. 4, the specific heat in zero-field also displays anomalies around T_{s1} and T_{s2}, indicting phase transitions at both temperatures. The applied magnetic field of 14 T increases T_{s1}, but depresses T_{s2} to lower temperature. Therefore, T_{s1} and T_{s2} can be related to a ferromagnetic and an antiferromagnetic phase transition, respectively. Around T_{s2}, the specific heat shows λ-like shape characteristic of a second order phase transition and confirms the bulk nature of the antiferromagnetic transition. Consistently, upon cooling the sample at 10 Oe to 4.5 K then warming back, no hysteresis of magnetization has been found around this temperature, see Fig. 5. The magnetization only displays hysteresis around T_{s1}, consistent with a first order structural transition as observed by Hsu et al. [6].

For α-FeSe, the stoichiometric sample is nonmagnetic [12, 14], both magnetism and superconductivity are driven by anion vacancy. If there is competition between magnetism and superconductivity, the applied pressure should suppress the magnetic transition, as expected by Margadonna et al. [13]. However, contrary to their expectation, the applied pressure not only increases T_c but also raises T_{s1} and T_{s2}, see Fig. 3. In addition, the specific heat anomaly associated with the superconducting transition in this material appears to be absent. By inspecting the inset of Fig. 4, T^2 dependence of C_p/T displays a traditional linear behavior for metal. The applied field of 14 T has also no evident influence on the specific heat around T_c. The absence of specific heat anomaly might imply non-bulk superconductivity for our sample. A small volume fraction of superconducting phase was also reported by other groups [7, 15], and has

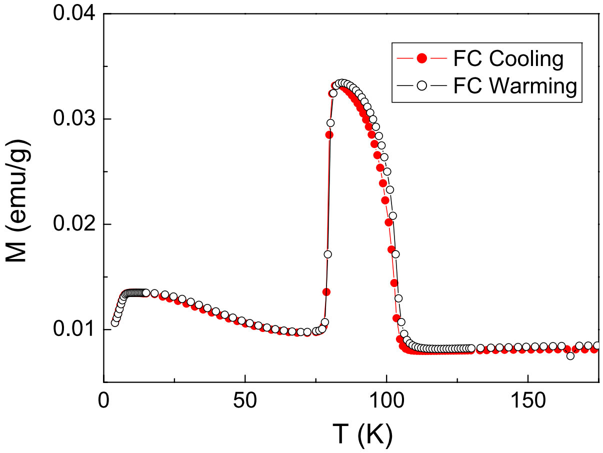

Fig. 5 FC magnetization curves for $x = 0.88$ with *solid circles* denoting field cooling and *open circles* denoting field warming sequence

been attributed to proximity effect between superconductivity and magnetism.

In conclusion, the pressure effect on magnetism and superconductivity has been studied in FeSe$_x$ ($x = 0.80, 0.88$). The magnetization and specific heat measurements show two magnetic phase transitions at T_{s1} and T_{s2}, respectively. The application of high pressure not only raises the superconducting critical temperature, but also intensifies the magnetic transitions.

Acknowledgements This research was financially supported by the National Key Basic Research of China Grant 2007CB925001, 2007CB925003, and the National Nature Science Foundation of China Grant 10774147, as well as Director's Fund of Hefei Institutes of Physical Science, Chinese Academy of Sciences.

References

1. Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H.: J. Am. Chem. Soc. **130**, 3296 (2008)
2. Chen, X.H., Wu, T., Wu, G., Liu, R.H., Chen, H., Fang, D.F.: Nature **453**, 761 (2008)
3. dela Cruz, C.R., Huang, Q., Lynn, J.W., Li, J., Ratcliff II, W., Zarestky, J.L., Mook, H.A., Chen, G.F., Luo, J.L., Wang, N.L., Dai, P.: Nature **453**, 899 (2008)
4. Klingeler, R., Leps, N., Hellmann, I., Popa, A., Hess, C., Kondrat, A., Hamann-Borrero, J., Behr, G., Kataev, V., Buechner, B.: arXiv:0808.0708v1 (2008)
5. Opahle, I., Kandpal, H.C., Zhang, Y., Gros, C., Valenti, R.: arXiv:0808.0834v1 (2008)
6. Hsu, F.C., Luo, J.Y., Yeh, K.W., Chen, T.K., Huang, T.W., Wu, P.M., Lee, Y.C., Huang, Y.L., Chu, Y.Y., Yan, D.C., Wu, M.K.: Proc. Natl. Acad. Sci. USA **105**, 14262 (2008)
7. Mizuguchi, Y., Tomioka, F., Tsuda, S., Yamaguchi, T., Takano, Y.: Appl. Phys. Lett. **93**, 152505 (2008)
8. Fang, M.H., Pham, H.M., Qian, B., Liu, T.J., Vehstedt, E.K., Liu, Y., Spinu, L., Mao, Z.Q.: Phys. Rev. B **78**, 224503 (2008)
9. Yeh, K.W., Huang, T.W., Huang, Y.L., Chen, T.K., Hsu, F.C., Wu, P.M., Lee, Y.C., Chu, Y.Y., Chen, C.L., Luo, J.Y., Yan, D.C., Wu, M.K.: arXiv:0808.0474 (2008)
10. Kotegawa, H., Masaki, S., Awai, Y., Tou, H., Mizuguchi, Y., Takano, Y.: arXiv:0808.0040v2 (2008)
11. Subedi, A., Zhang, L., Singh, D.J., Du, M.H.: Phys. Rev. B **78**, 134514 (2008)
12. Lee, K.W., Pardo, V., Pickett, W.E.: Phys. Rev. B **78**, 174502 (2008)
13. Margadonna, S., Takabayashi, Y., McDonald, M.T., Kasperkiewicz, K., Mizuguchi, Y., Takano, Y., Fitch, A.N., Suard, E., Prassides, K.: arXiv:0807.4610 (2008)
14. Wu, X.J., Zhang, Z.Z., Zhang, J.Y., Li, B.H., Ju, Z.G., Lu, Y.M., Li, B.S., Shen, D.Z.: J. Appl. Phys. **103**, 113501 (2008)
15. Fang, M.H., Qian, B., Pham, H.M., Yang, J.H., Liu, T.J., Vehstedt, E.K., Spinu, L., Mao, Z.Q.: arXiv:0811.3021 (2008)