Micro-Raman and infrared study of NdFeAsO$_{0.85}$

E. Siranidi [a,*], D. Lampakis [a], E. Liarokapis [a], Z. Dohcevic-Mitrovic [b], N. Paunovic [b], Z.V. Popovic [b], Z.X. Zhao [c]

[a] Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece
[b] Center for Solid State Physics and New Materials, Institute of Physics, Pregrevica 118, 11080 Belgrade, SerbiaSerbia
[c] National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, PR China

ARTICLE INFO

ABSTRACT

We report micro-Raman and infrared measurements on high quality iron-based arsenic oxide, at low temperatures (down to 20 K). Micro-Raman spectra exhibit two asymmetric peaks related to four phonon modes of As, Fe at ~160 cm^{-1}, of Nd at ~169 cm^{-1}, of As at ~203 cm^{-1} and of Fe at ~214 cm^{-1}. No phonon anomaly has been observed at the superconducting transition. Far infrared reflectance measurements were performed at low temperatures, down to 77 K. In the far IR spectra obtained at room temperature, there are two strong peaks at about ~105 cm^{-1} (13 meV), and ~446 cm^{-1} (55 meV) and one weaker structure around ~270 cm^{-1} (33.4 meV). The assignment of the observed modes has been done. Additionally, a band at ~494 cm^{-1} and for temperatures below 230 K a peak at ~200 cm^{-1} were observed. The temperature dependence of these modes reveals an unconventional behavior of the IR modes not reported before.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The recently discovery of superconductivity in a non-copper oxide based layered compound attracted a lot of attention on this new class of materials belonging to the family of iron oxypnictides [1]. Soon after the first report, about the superconductivity in LaFeAsO$_{1-x}$F$_x$ with T_c = 26 K, the rare-earth substitution compounds with general type ReFeAsO$_{1-x}$F$_x$ (Re= Sm, Nd, Ce, Pr, Gd) were synthesized with even higher T_c [2–6].

The ReFeAsO compounds have a layered structure of alternating Fe–As and Re–O layers. The undoped compound is not a superconductor and a spin density wave (SDW) order has been reported for temperatures below ~150 K [7]. However, neutron diffraction study of the polycrystalline non-superconducting LaFeAsO shows that the resistivity anomaly at 150 K is caused by the structural distortion that occurs at the compound and not by the SDW ordering [8]. Upon fluorine doping on the oxygen site or with oxygen vacancies [9] the SDW [7] or the structural distortion [8] suppresses in favor of superconductivity. Furthermore, superconductivity can be induced by the substitution of thorium [10] (electron doping) or strontium [11] (hole doping) on the rare-earth site. In addition,

recently it was shown that superconductivity can be achieved not only with doping in the LaO layers but also with the substitution of Fe by Co or Ni [12,13], whereas, the Mn doping in the FeAs layer does not induce superconductivity but leads to a metal-semiconductor transition [14].

Despite the plethora of the experimental and theoretical reports about oxypnictides, it is still controversial which is the mechanism that leads to the superconductivity in these systems. Raman spectroscopy, although probes only the $q \cong 0$ phonons in the Brillouin zone, can provide direct and reliable evidence about small lattice distortions and therefore detects a possible weak interaction of the lattice with the charge or spin ordering. Furthermore, infrared spectroscopy can provide information about the electronic properties of the system. Therefore, a combination of these two techniques can contribute to the better understanding of the mechanism that gives rise to superconductivity in these systems. In this work we report systematic Raman and infrared measurements on high quality iron-based arsenic oxide NdFeAsO$_{0.85}$ without F doping, at low temperatures (down to 20 K) in order to detect any possible phonon anomalies at the superconducting state.

2. Experimental

Polycrystalline compound of NdFeAsO$_{0.85}$ with T_c = 53.5 K [9] has been examined using micro-Raman and infrared spectroscopy. The preparation of the sample is described elsewhere [5]. Typical size of the microcrystals was of few 2–3 μm.

* Corresponding author. Tel.: +30 210 7722950; fax: +30 210 7723312.
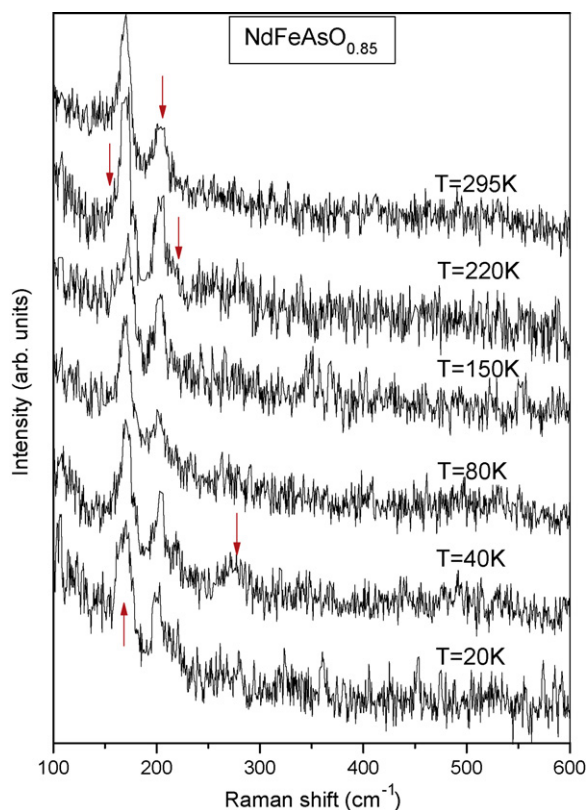*E-mail address:* esiran@central.ntua.gr (E. Siranidi).

Fig. 1. Typical Raman spectra at different temperatures of the NdFeAsO$_{0.85}$ compound collected from the polished surface of the sample using the 514.5 nm excitation wavelength.
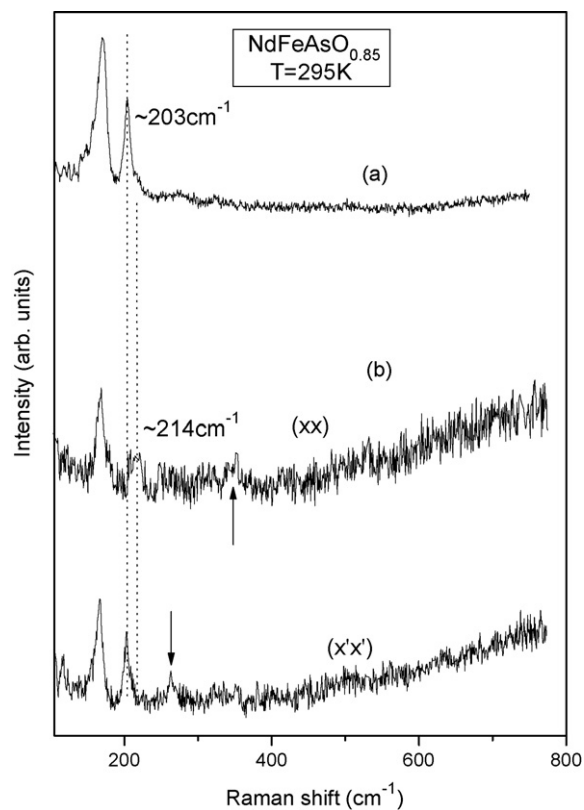

Fig. 2. Raman spectra at room temperature for the NdFeAsO$_{0.85}$ compound collected from (a) the polished surface of the sample and (b) one microcrystal measured in the xx (upper panel) and $x'x'$ (lower panel) polarization.
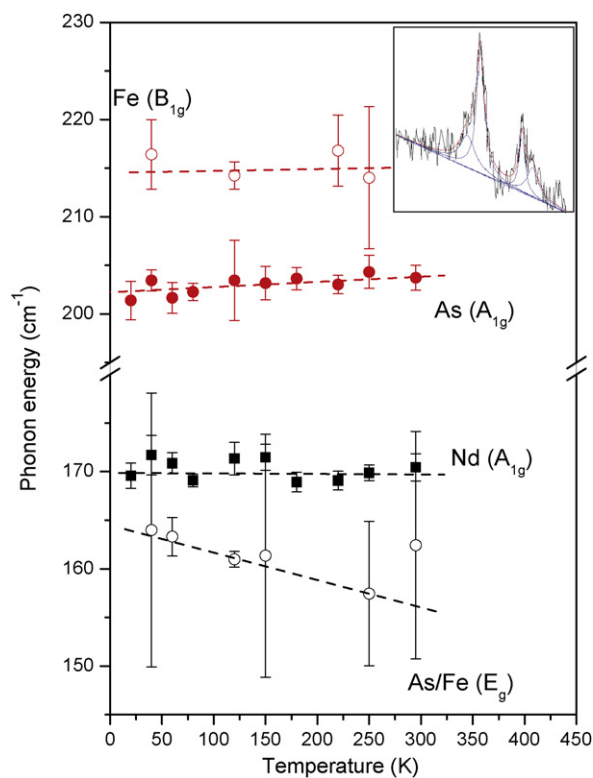

Fig. 3. Temperature dependence of the four Raman active modes which appear at all temperatures under study. Inset: the fitting result of the two asymmetric peaks using two Lorentzian curves for each peak. Dashed lines are linear fit to the data.

The sample was pressed into a pellet and then polished to obtain flat and shiny surface for the Raman and infrared measurements. All Raman measurements, including the low temperature ones, were performed in a micro-Raman set-up using a Jobin-Yvon T64000 triple spectrometer equipped with a liquid nitrogen cooled CCD and a microscope (magnification 100×). The excitation line was 514.5 nm of an Ar$^+$ laser and was kept at very low power level (less than 10 kW/cm^2) securing low heating of the compound. The maximum temperature rise due to the laser beam has been estimated to be less than 10 K [15]. Low temperatures were achieved using an open cycle Oxford CF1104 cryostat operating with liquid nitrogen and liquid helium. During the low-temperature measurements obtained from the polished surface of the compound we kept the same spot with the same orientation of the sample so as to keep the same polarization at all temperatures under study. The infrared measurements were carried out on a BOMEM DA-8 FTIR spectrometer. A DTGS pyroelectric detector was used for the wave number region from 40 cm^{-1} to 700 cm^{-1}; a liquid nitrogen cooled HgCdTe detector was used from 400 cm^{-1} to 4000 cm^{-1}. Reflectivity spectra were collected with 2 cm^{-1} resolution, with 500 interferometer scans added for each spectrum. For low-temperature measurements a Janis STDA 100 cryostat was used.

3. Results and discussion

3.1. Raman measurements

NdFeAsO$_{0.85}$ crystallizes in the P$_{4/nmm}$ structure [1,2] and according to the factor group analysis there are eight Raman 2A$_{1g}$ + 2B$_{1g}$ + 4E$_g$ and six infrared 3A$_{2u}$ + 3E$_u$ active modes. Typical Raman spectra at selected temperatures, obtained from the polished surface of the compound are presented in Fig. 1. Fig. 2a shows the spectrum of NdFeAsO$_{0.85}$ compound at room temperature, also obtained from the polished surface of the compound whereas in Fig. 2b the spectra of one microcrystal, collected from the unpolished surface of the compound, at room temperature in the xx (upper panel) and $x'x'$ (lower panel) scattering geometries are shown.

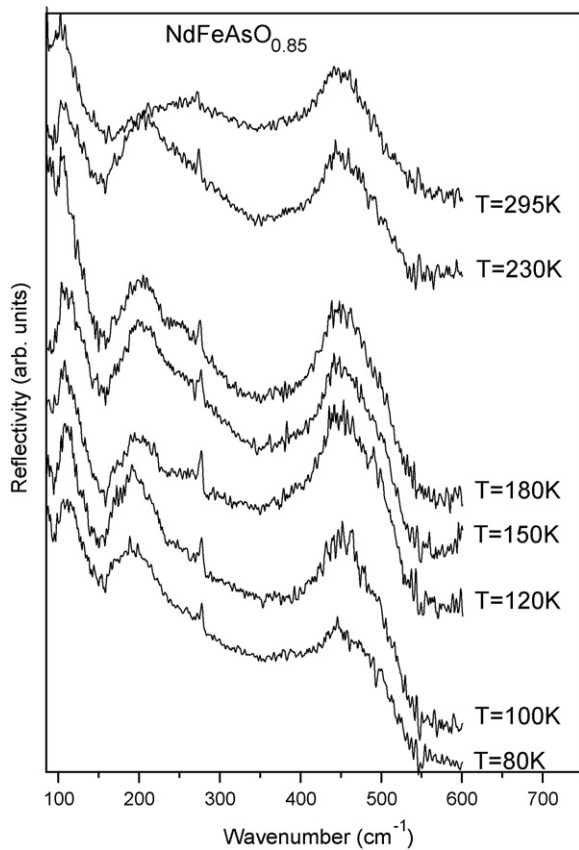In Fig. 1 only two asymmetric peaks at ∼169 cm^{-1} and ∼203 cm^{-1} are observed at all temperature under study. With

Fig. 4. Typical IR spectra of NdFeAsO$_{0.85}$ at different temperatures.

further temperature decrease down to 40 K, another band at ~278 cm^{-1} appears in the Raman spectra. However, in Fig. 2b where the xx and $x'x'$ polarizations of the NdFeAsO$_{0.85}$ compound are presented, it is easily observed that in the upper spectrum there is a peak at ~214 cm^{-1}, whereas in the lower one there is a band peaked at ~203 cm^{-1}. Since, the low-temperature spectra presented in Fig. 1 were collected from the polished surface of the sample, we cannot be certain about the selection rules. Therefore, we believe that the two observed asymmetric peaks are related to four Raman active modes. Based on the assignment done for the RFeAsO family of compounds we conclude that the mode observed at ~160 cm^{-1} is of E$_g$-symmetry and is probably connected to the vibrations of As, Fe atoms [16–18], the modes at ~169 cm^{-1} and ~203 cm^{-1} are of A$_{1g}$-symmetry and are related to the vibrations of Nd and As atoms, respectively and finally the mode at ~214 cm^{-1} is the B$_{1g}$-symmetry mode of Fe atoms [16–20]. The peak that appears at ~278 cm^{-1} is also related to the Fe vibrations and is of E$_g$-symmetry [16–18]. Furthermore, in the upper panel of Fig. 2b there is a band peaked at ~347 cm^{-1} which is of B$_{1g}$-symmetry related to the vibrations of oxygen atoms [17–20]. The fact that this peak is observed only when the peak at ~214 cm^{-1} appears, is in agreement with our assignment that both of these peaks are of B$_{1g}$ symmetry. No sign of the E$_g$-symmetry phonons of the Nd and oxygen atoms has been observed.

Fig. 3 presents the frequency vs. temperature dependence of the two asymmetric modes that appear in the Raman spectra of Fig. 1 at all temperatures under study. The phonon peaks were fitted using two Lorentzian curves in order to see the energy shift of all four modes. The A$_{1g}$-symmetry modes of Nd and As are almost independent of temperature, in disagreement with the results of Refs. [18,20] where phonon softening with increasing temperature was observed. Concerning the E$_g$ and B$_{1g}$-symmetry phonons at

~160 cm^{-1} and 214 cm^{-1}, the big uncertainty of their energy do not allow us to make any safe conclusions about their temperature dependence. No phonon anomaly across T_c has been detected. Besides, no spectral modifications are observed at temperatures below the superconducting transition temperature. Considering the polycrystalline nature of the sample which has random orientations of the c-axis and the ab-planes, the absence of any new phonon mode below T_c, as expected, indicates that there is no lattice distortion across the superconducting transition.

3.2. Infrared measurements

Fig. 4 shows the low-temperature unpolarized reflectivity spectra of NdFeAsO$_{0.85}$ in the far infrared energy region (40–700 cm^{-1}). The high reflectivity signal proves the good metallic behavior of the compound, which persists at all temperatures studied (down to 77 K). In the far IR spectra at room temperature, where most of the phonon modes are expected to appear, there are two strong peaks at about ~105 cm^{-1} (13 meV) and ~446 cm^{-1} (55 meV) and one weaker structure around ~270 cm^{-1} (33.4 meV). The positions of these peaks are in full agreement with the infrared spectroscopic data of CeO$_{1-x}$F$_x$FeAs [3], LaO$_{0.9}$F$_{0.1}$FeAs [21], LaO$_{1-x}$F$_x$FeAs [7] and (Nd,Sm)FeAsO$_{0.82}$F$_{0.18}$[22]. However, the high energy band at ~446 cm^{-1} is very broad and asymmetric, indicating that it is not consisted of only one peak, as reported before [17,21,23], but a second peak at ~494 cm^{-1} also appears. The peak at ~105 cm^{-1} is probably related to vibrations of Nd atoms, whereas the mode which appears at ~270 cm^{-1} is correlated to the vibrations of either the Fe, As atoms or the O atoms [16,17]. The high energy modes at ~446 cm^{-1} and ~494 cm^{-1} are presumably related to the vibrations of oxygen atoms, since at such high frequencies only these phonon modes are expected to appear [21]. The two strong peaks observed at ~105 cm^{-1} and ~446 cm^{-1} must correspond to phonons polarized along the c-axis of the lattice, since screening effects are less
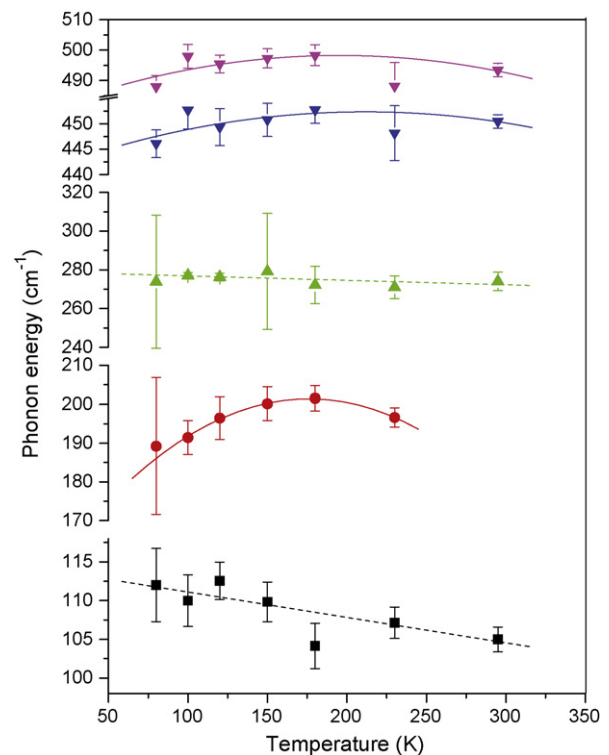

Fig. 5. Temperature dependence of the modes that appear in the far IR reflectivity spectra. Dashed lines are linear fit and solid lines are second order polynomial fit to the data.

intense in this direction, in agreement with Ref. [21]. At low temperatures (T $\leq$ 230 K) an extra band appears in the far infrared region at $\sim$200 cm^{-1}. The origin of this mode is still unclear since no IR mode is expected to appear in this energy region [16,17] and has never been observed before in the infrared spectra of the RFeAsO family of compounds [3,7,24]. Repeated polishing of the sample did not induce any change in the IR spectra, indicating that the origin of the peak at $\sim$200 cm^{-1} is related to the NdFeAsO$_{0.85}$ phase.

The energy vs. temperature dependence of the strong mode at $\sim$105 cm^{-1}, which appears in the far IR reflectivity spectra presented in Fig. 4, displays a slight decrease in energy with increasing temperature, as expected. The mode at $\sim$270 cm^{-1} is almost temperature independent whereas the peaks at $\sim$200 cm^{-1}, $\sim$446 cm^{-1}, and $\sim$494 cm^{-1} show an abnormal phonon temperature dependence; their energy increases with increasing temperature up to $\sim$180 K and then it decreases until room temperature (Fig. 5). The effect is more intense for the peak at $\sim$200 cm^{-1}. The peculiar behavior of these modes has never been observed up to now and it requires further investigation to reveal its origin.

4. Conclusions

In this work Raman and IR reflectivity measurements of the recently discovered iron-based superconductor without F doping with general type NdFeAsO$_{0.85}$ have been performed. The observed modes have been assigned accordingly. The temperature dependence of the Raman active phonon modes proves that there is no phonon softening or any anomaly across T_c. However, in the IR spectra a band at $\sim$494 cm^{-1}, and at low temperatures a mode at $\sim$200 cm^{-1} were observed, that have never been reported before. The analysis of the data revealed an unconventional behavior of the IR modes with temperature.

Acknowledgements

References

[1] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, J. Am. Chem. Soc. 130 (2008) 3296.
[2] X.H. Chen, T. Wu, G. Wu, R.H. Liu, H. Chen, D.F. Fang, Nature 453 (2008) 761.
[3] G.F. Chen, Z. Li, G. Wu, G. Li, W.Z. Hu, J. Dong, P. Zheng, J.L. Luo, N.L. Wang, Phys. Rev. Lett. 100 (2008) 247002.
[4] J. Yang, Z. Li, W. Lu, W. Yi, X.L. Shen, Z.A. Ren, G.C. Che, X.L. Dong, L.L. Sun, F. Zhou, Z.X. Zhao, Supercond. Sci. Technol. 21 (2008) 082001.
[5] Z.A. Ren, J. Yang, W. Lu, W. Yi, G.C. Che, X.L. Dong, L.L. Sun, Z.X. Zhao, Mater. Res. Innov. 12 (2008) 105.
[6] Z.A. Ren, J. Yang, W. Lu, W. Yi, X.L. Shen, Z.C. Li, G.C. Che, X.L. Dong, L.L. Sun, F. Zhou, Z.X. Zhao, Europhys. Lett. 82 (2008) 57002.
[7] 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.
[8] C. Cruz, Q. Huang, J.W. Lynn, J.Y. Li, W. Ratcliff, J.L. Zarestky, H.A. Mook, G.G. Chen, J.L. Luo, N.L. Wang, P.C. Dai II, Nature 453 (2008) 899.
[9] Z.A. Ren, G.C. Che, X.L. Dong, J. Yang, W. Lu, W. Yi, X.L. Shen, Z.C. Li, L.L. Sun, F. Zhou, Z.X. Zhao, Europhys. Lett. 83 (2008) 17002.
[10] C. Wang, L. Li, S. Chi, Z. Zhu, Z. Ren, Y. Li, Y. Wang, X. Lin, Y. Luo, S. Jiang, X. Xu, G. Cao, Z. Xu, Europhys. Lett. 83 (2008) 67006.
[11] H.H. Wen, G. Mu, L. Fang, H. Yang, X. Zhu, Europhys. Lett. 82 (2008) 17009.
[12] 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.
[13] G. Cao, S. Jiang, X. Lin, C. Wang, Y. Li, Z. Ren, Q. Tao, C. Feng, J. Dai, Z. Xu, F.C. Zhang, Phys. Rev. B 79 (2009) 174505.
[14] D. Bérandan, L. Pinsard-Gaudart, N. Dragoe, J. Alloys Compd. 481 (2009) 470.
[15] M. Lax, J. Appl. Phys. 48 (1977) 3919.
[16] S.C. Zhao, D. Hou, Y. Wu, Y.L. Xia, A.M. Zhang, G.F. Chen, J.L. Luo, N.L. Wang, J.H. Wei, Z.Y. Lu, Q.M. Zhang, Supercond. Sci. Technol. 22 (2009) 015017.
[17] C. Marini, C. Mirri, G. Profeta, S. Lupi, D. Di Castro, R. Sopracase, P. Postorino, P. Calvani, A. Perucchi, S. Massidda, G.M. Tropeano, M. Putti, A. Martinelli, A. Palenzona, P. Dore, Europhys. Lett. 84 (2008) 67013.
[18] L. Zhang, T. Fujita, F. Chen, D.L. Feng, S. Maekawa, M.W. Chen, Phys. Rev. B 79 (2009) 052507.
[19] V.G. Hadjiev, M.N. Iliev, K. Sasmal, Y.Y. Sun, C.W. Chu, Phys. Rev. B 77 (2008) 220505(R).
[20] Y. Gallais, A. Sacuto, M. Cazayous, P. Cheng, L. Fang, H.H. Wen, Phys. Rev. B 78 (2008) 132509.
[21] S.L. Drechsler, M. Grobosch, K. Koepernik, G. Behr, A. Köhler, J. Werner, A. Kondrat, N. Leps, Ch. Hess, R. Klingeler, R. Schuster, B. Büchner, M. Knupfer, Phys. Rev. Lett. 101 (2008) 257004.
[22] A. Dubroka, K.W. Kim, M. Rössle, V.K. Malik, A.J. Drew, R.H. Liu, G. Wu, X.H. Chen, C. Bernhard, Phys. Rev. Lett. 101 (2008) 097011.
[23] M. Tropeano, C. Fanciulli, C. Ferdeghini, D. Marrè, A.S. Siri, M. Putti, A. Martinelli, M. Ferretti, A. Palenzona, M.R. Cimberle, C. Mirri, S. Lupi, R. Sopracase, P. Calvani, A. Perucchi, Superond. Sci. Technol. 22 (2009) 034004.
[24] G.F. Chen, Z. Li, G. Li, J. Zhou, D. Wu, J. Dong, W.Z. Hu, P. Zheng, Z.J. Chen, H.Q. Yuan, J. Singleton, J.L. Luo, N.L. Wang, Phys. Rev. Lett. 101 (2008) 057007.