Cent. Eur. J. Phys. • 7(2) • 2009 • 251-256
DOI: 10.2478/s11534-009-0017-9

VERSITA

Central European Journal of **Physics**

Two-gap superconductivity in the Fe-1111 superconductor $LaFeAsO_{1-x}F_x$: A point-contact Andreev-reflection study

Research Article

Renato S. Gonnelli[1]*, Mauro Tortello[1], Dario Daghero[1], Giovanni Alberto Ummarino[1], Valeri A. Stepanov[2], Jun S. Kim[3]

1 *Dipartimento di Fisica and CNISM, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy*

2 *P. N. Lebedev Physical Institute, Russian Academy of Sciences, Leninskiy Prospekt 53, 119991, Moscow, Russia*

3 *Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany,*

Received 5 December 2008; accepted 25 February 2009

Abstract: Point-contact Andreev-reflection (PCAR) experiments were performed in the Fe-1111 layered superconductor $LaFeAsO_{0.9}F_{0.1}$ with resistive $T_c^{on} \sim 27$ K. The observation of two pairs of peaks in the low-temperature Andreev-reflection spectra clearly indicates the presence of two order parameters. The behavior of the two gaps as a function of temperature, obtained by fitting the conductance curves by means of the generalized two-band Blonder-Tinkham-Klapwijk model, shows some anomalies. A theoretical analysis performed within the two-band Eliashberg theory with a generic electron-boson coupling can reproduce the low-temperature value of the two gaps but generally fails in giving a satisfactory fit of their overall temperature dependence, indicating the rich and complex physics of these newly discovered superconductors.

PACS (2008): 74.45.+c; 74.50.+r; 74.70.Dd

Keywords: Fe-based superconductors • point-contact Andreev-reflection spectroscopy • two-band Eliashberg theory

1. Introduction

In January 2008, Kamihara *et al.* showed that the quaternary oxypnictide LaFeAsO becomes superconducting with $T_c \sim 26$ K upon F doping [1]. This report attracted the attention of several chemists and physicists and, a few weeks later, the critical temperature of the compound was increased up to 43 K by pressure [2] and above 50 K by substituting La with other rare-earth elements such as Sm, Pr, Nd [3–5]. It was also shown that oxygen deficiency has the same effect as F doping [6]. As in cuprate superconductors, superconductivity in LaFeAsO occurs upon charge doping of the magnetic parent compound above a certain critical value. However, while in the case of cuprates the parent compound is a Mott insulator with localized charge carriers and a strong Coulomb repulsion between electrons, LaFeAsO is rather metallic and shows an antiferromagnetic spin-density-wave (SDW) order below ~ 140 K which follows a tetragonal to orthorhombic

*E-mail: renato.gonnelli@polito.it

structural transition [7]. Charge doping disrupts both the magnetic order and the structural transition, leading to the appearance of superconductivity in the FeAs planes. $LaFeAsO_{1-x}F_x$ belongs to the so called "1111" structure (from its formula unit). Different systems of Fe-based superconductors have also been discovered such as the "122" structure which shows T_c up to 38 K in doped AFe_2As_2 (A=Ba, Sr, Ca, Eu) [8, 9] or the "111" structure with T_c = 18 K in the LiFeAs system. The simplest Fe-based superconductor is the tetragonal "11" FeSe with T_c = 8 K [10] that can be increased up to 27 K under pressure [11].

The high critical temperatures (several Fe-based superconductors feature the highest T_c known so far with the exception of the cuprates), the vicinity of the superconducting state to a magnetic parent compound, the intriguing similarities and differences with the copper-based superconductors have attracted the attention of the scientific community. At present, major efforts are devoted to clarify the pairing mechanism that gives rise to superconductivity, and its relationship with magnetism. Density functional perturbation theory showed that the electron-phonon coupling seems not to be sufficient to reproduce the observed T_c [12]. At the same time, a coupling mediated by antiferromagnetic spin fluctuations has been proposed, that predicts an extended *s*-wave symmetry ($s\pm$) for the superconducting order parameter [13]. In this context, experiments able to directly measure the superconducting energy gap (s), and to determine its (their) symmetry are eagerly awaited. Spectroscopic techniques such as ARPES or STM/STS need single crystal specimen which are not yet available for all the Fe-based compounds. Point-contact Andreev-reflection spectroscopy (PCAR) measurements, instead, can be performed also on polycrystalline samples.

Here we report on PCAR measurements performed in polycrystalline samples of $LaFeAsO_{1-x}F_x$ with critical temperature (defined at 90% of the resistive transition) T_c^{on}= 27 K, and a transition width ΔT_c = 4 K. We will show that PCAR gives clear evidence for two order parameters. The trend of the two gaps as a function of the temperature, which is rather unconventional, is discussed within the two-band Eliashberg model.

2. Experimental

The polycrystalline samples were prepared according to the method reported in Ref. [14] by solid state reaction and by using LaAs, FeO_3, Fe and LaF_3 as starting materials. The nominal composition was $LaFeAsO_{0.9}F_{0.1}$ and samples exhibited the onset of the resistive transition at T_c^{on} = 27 K. They are made up of different crystallites in a more disordered matrix; the F content is homogeneous inside each crystallite, although it can vary from one crystallite to another within Δx = 0.02 as revealed by micro EDX (energy-dispersive X-ray spectroscopy). The slight variation of the F content is not an obstacle to our measurements. The only consequence is that, since PCAR spectroscopy is a local surface-sensitive technique, slight variations in the critical temperature and in the measured gap amplitude(s) are expected from one contact to another.

The point contacts were made with the so-called "soft" technique that consists in using, instead of the standard metallic tip pressed against the sample, a small drop of Ag conductive paste directly put on the freshly cleaved surface [15, 16]. In this way, no pressure is applied to the sample under study, and the measurements are highly repeatable even under thermal cycling. The potential barrier at the N/S interface is usually small and the contacts are thus mainly in the Andreev-reflection regime [17]. When the size of the contact is small with respect to the electron mean free path ℓ in the superconductor (ballistic contact) it is possible to obtain information about the superconducting gap from the I-V characteristic of the junction or, better, from its differential conductance dI/dV. At the present stage of knowledge, the value of ℓ in these compounds is still unknown (and may strongly depend on the quality of the samples that has still to be optimized). However, the clear Andreev-reflection features shown in our measured conductances (obtained by taking the numerical derivative of the I-V characteristics), as well as the absence of heating effects and of dips, indicate that our contacts are in the ballistic regime and the spectroscopic requirements are satisfied. In fact, according to Ref. [18], the presence of dips in the conductance curves of point contacts is a hallmark of the breakdown of the conditions for ballistic conduction at finite voltage and signals the presence of heating in the contact region. This effect is totally absent here thus confirming that the conditions for ballistic conduction are fully satisfied. Blonder, Tinkham and Klapwijk (BTK) proposed a theoretical model that can be used to determine the value of the gap from the conductance measured in ballistic contacts in the tunneling or in the Andreev-reflection regime [19]. In order to compare the experimental results with the BTK model the conductances must be "normalized", *i.e.* divided by their normal-state value. In our case we actually used a two-band modified [20] BTK model generalized to the 3D case [22]. In this two-band case the normalized conductance is the weighed sum of the BTK conductance of each band, $G(V) = w_1 G_1(V) + (1 - w_1) G_2(V)$. The conductance in each band is completely defined by three parameters: the amplitude of the order parameter,

Δ, a broadening parameter, Γ [20], and the effective barrier parameter Z, which accounts for the height of the potential barrier and the mismatch of the Fermi velocities at the N/S interface.

3. Results and discussion

Fig. 1 a) reports an example of the temperature dependence of raw conductance curves measured in a point contact on $LaFeAsO_{1-x}F_x$. The low-temperature curve clearly features two pairs of peaks (indicated by arrows) at about $\pm$ 2 mV and $\pm$ 8.5 mV, respectively, possibly indicating the presence of two superconducting order parameters. In addition, a systematic asymmetry of the conductance is observed, which is probably related to the fast decrease in the density of states on crossing the Fermi level and is common to all point-contact and tunnel spectra measured in Fe-As-based superconductors [21].

The Andreev-reflection features decrease in amplitude with increasing temperature until they completely disappear at the critical temperature of the junction, which, for the case shown in the figure, is T_c = 28.6 K. Due to the slightly different F content from one crystallite to another, we could also observe critical temperatures slightly higher than the bulk one. It is worth noticing that critical temperatures higher than 28 K for this compound have been indeed reported in literature in the case of samples synthesized under high pressure [23] or with oxygen deficiencies [6]. In particular, the latter possibility cannot be completely excluded in our samples.

The normal-state conductance (curve at T=28.6 K) shows a depression around zero bias which is related to the presence of pseudogap-like features [24]. We can reasonably rule out an extrinsic origin for these features due, for example, to the presence of some non-metallic (semiconducting) contacts parallel to the superconducting ones. In fact the parent undoped and non-superconducting compound is a bad metal and the SEM and micro EDX measurements performed on this sample gave no evidence of non-conducting regions on the sample surface. In addition, the pseudogap-like behaviour is present also in the superconducting state and gradually fills with increasing temperature until it completely disappears at about the Néel temperature of the parent compound, $T_N \sim$ 140 K [7]. It therefore affects the conductance curves also in the superconducting state. Since the normal-state conductance at low temperature is not accessible, the conductance curves were normalized as reported in Ref. [24], *i.e.* by means of a B-spline curve which interpolates the "tails" of the conductance at high

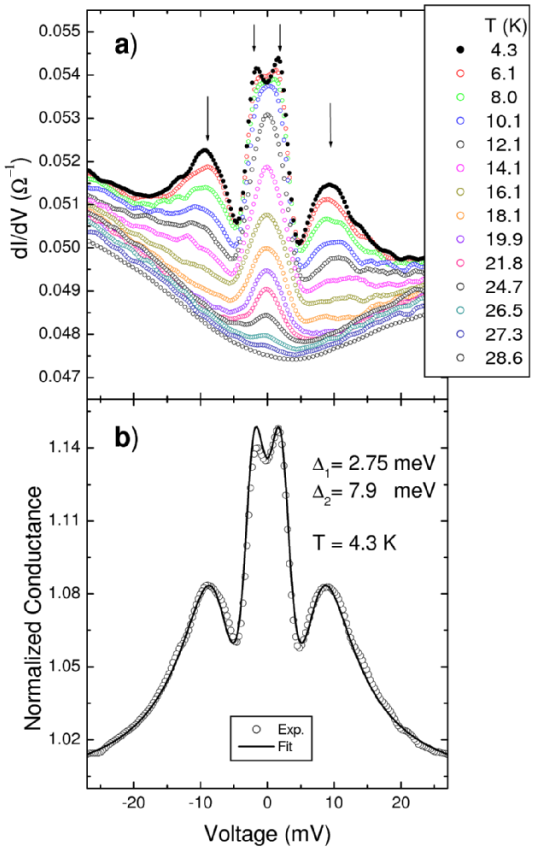

Figure 1. a): Temperature dependence of the raw conductance curves measured in a point contact on $LaFeAsO_{0.9}F_{0.1}$. The low-temperature curve clearly shows the structures related to the two order parameters (indicated by arrows). The critical temperature of the junction was 28.6 K. b): Low-temperature normalized curve (symbols) of the point-contact measurement reported in panel a). The solid line is a two-band BTK fit to the experimental curve. The obtained gap values are Δ_1 = 2.75 meV and Δ_2 = 7.90 meV.

energies and is connected to a suitable point at zero bias that simulates the dip due to the conductance depression. As shown in detail in Ref. [24], this method provides a good tool for the normalization, but one could use as well another approach - for example dividing the conductance curve by the normal-state one measured just above T_c. It can be shown that the choice of the normalization is not crucial for the results, since it gives rise to variations within 10% for the large gap, Δ_2, and 1.5 % for the small one, Δ_1.

Fig. 1 b) reports the normalized low-temperature curve obtained from the data at 4.3 K shown in panel a). From the two-band BTK fit, values of Δ_1 = 2.75 meV and Δ_2 = 7.90 meV were obtained for the small and the large gap, respectively. The other fitting parameters are

$\Gamma_1 = 0.93$ meV, $\Gamma_2 = 3.90$ meV, $Z_1 = 0.21$ and $Z_2 = 0.93$. Notice that the Γ parameters are smaller ($\leq 50\%$) than the corresponding gap values, thus indicating the presence of a good Andreev-reflection signal.

From the two-band BTK fit of all the conductance curves reported in Fig. 1 a) (of course after normalization), we could obtain the evolution of the gaps as a function of temperature. The result is shown in Fig. 2 a) (symbols). It is possible to see that the large gap, Δ_2, approximately follows a BCS-like behaviour but, apparently, it closes below the critical temperature of the junction. The small gap, Δ_1, features instead a rather anomalous behavior above $\sim T_c/2$ and closes at T_c with a sort of tail-like shape.

The behavior of the gaps here presented is rather unconventional and needs to be studied more deeply. In particular it could help clarifying the possible unconventional physics of these newly discovered superconductors.

As far as the small gap, Δ_1, is concerned, its temperature dependence resembles that of a proximized gap. One could thus argue that Δ_2 is the true order parameter while Δ_1 is the gap induced by proximity (for example in a normal surface layer). However, this is likely not to be the case, since Δ_2 either closes at a critical temperature $T^* \sim 23 - 24$ K $< T_c$, or follows the same tail-like behavior (the experimental resolution does not allow us to distinguish between these two possibilities).

Another possible interpretation of the temperature dependence of Δ_1 (at least from the phenomenological point of view) can be given within the standard *s*-wave two-band model for superconductivity. As a matter of fact, a similar behavior can be obtained for the small gap if one supposes the interband coupling be rather small, and the intraband coupling be larger in band 2 than in band 1 [25]. In the present case, the large value $2\Delta_2/k_B T_c = 6.42$ indicates that the problem should be discussed within the Eliashberg model for strong coupling superconductors.

Let us start from the generalization of the Eliashberg theory for *s*-wave two-band systems that has already been used with success to study the MgB_2 superconductor [26]. To obtain the gaps and the critical temperature within the two-band Eliashberg model one has to solve four coupled integral equations for the gaps $\Delta_i(i\omega_n)$ and the renormalization functions $Z_i(i\omega_n)$, where i is a band index ($i = 1$, 2) and ω_n are the Matsubara frequencies. At the present stage of knowledge we are not able to make any special hypothesis about the pairing mechanism (phonon, spin fluctuations or excitons) and thus we treat here the coupling in a very phenomenological way, by simply specifying some representative boson frequencies and some electron-boson coupling constants.

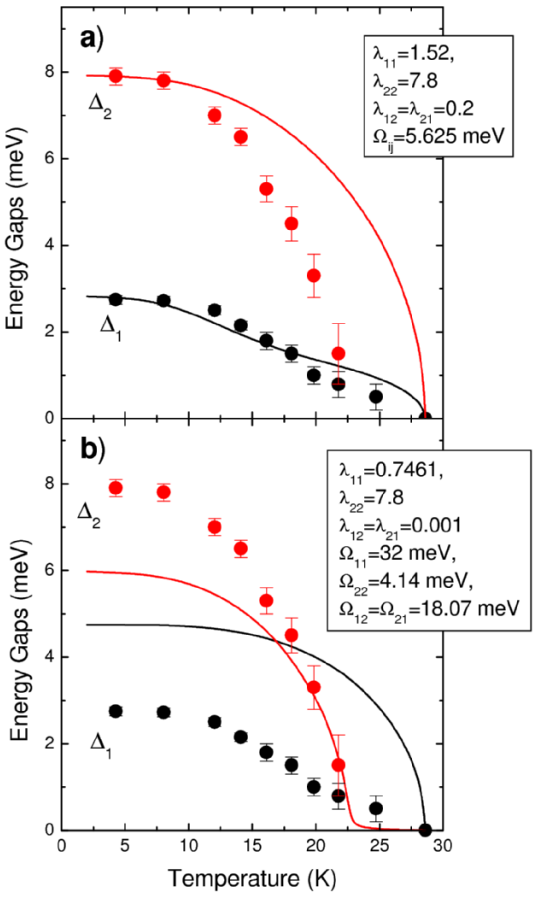

Figure 2. a): Temperature dependence of the gaps (symbols) obtained by the two-band BTK fit of the conductance curves reported in Fig. 1 a). Lines are theoretical curves calculated within the two-band Eliashberg theory by using the parameters reported in the inset (see text for further details). b): The same as in a) but the theoretical curves are calculated by using the parameters reported in the relevant inset.

The solution of the Eliashberg equations requires i) the four electron-boson spectral functions $\alpha^2_{ij}(\Omega)F(\Omega)$; ii) the four elements of the Coulomb pseudopotential matrix $\mu^*_{ij}(\omega_c)$; iii) the four non-magnetic impurity scattering rates Γ^N_{ij}; iv) the four paramagnetic impurity scattering rates Γ^M_{ij}. For the spectral functions we assume the following expression:

$$\alpha^2_{ij}(\Omega)F(\Omega) = \frac{C_{ij}}{\pi}\left[\frac{1}{(\Omega-\Omega_{ij})^2+(\Upsilon_{ij})^2} - \frac{1}{(\Omega+\Omega_{ij})^2+(\Upsilon_{ij})^2}\right], \quad (1)$$

where C_{ij} are the appropriate normalization constants necessary to obtain the proper values of λ_{ij}. By using,

for the electron-boson coupling constants, $\lambda_{11} = 1.52$, $\lambda_{22} = 7.80$, $\lambda_{12} = \lambda_{21} = 0.20$, and, for the characteristic boson frequencies, $\Omega_{ii} = \Omega_{ij} = \Omega_{jj} = 5.625$ meV, we obtain the result shown in Fig. 2 a) (solid lines). The other parameters used in the calculation were a cutoff frequency $\omega_c = 300$ meV, $\Upsilon_{ii} = \Upsilon_{ij} = \Upsilon_{jj} = 1$ meV, $\mu^*_{ii}(\omega_c) = \mu^*_{ij}(\omega_c) = \mu^*_{jj}(\omega_c) = 0$, and $\Gamma^{N,M}_{i,i} = \Gamma^{N,M}_{i,j} = \Gamma^{N,M}_{j,j} = 0$. In this case, the model gives the correct low-temperature value for both gaps and can moreover fit qualitatively well the temperature behavior of Δ_1, but fails in reproducing that of Δ_2.

If we try to reproduce the apparent closing of Δ_2 below T_c, the result is even poorer: by setting $\lambda_{11} = 0.746$, $\lambda_{22} = 7.800$, $\lambda_{12} = \lambda_{21} = 0.001$, and $\Omega_{11} = 32.00$ meV, $\Omega_{22} = 4.14$ meV, and $\Omega_{12} = \Omega_{21} = 18.07$ meV, we obtain the curves reported in Fig. 2 b) (the remaining parameters are the same as in the previous case). In this case, only a qualitative behavior for Δ_2 can be obtained: Δ_2, by itself, would close at a temperature $T^* < T_c$ but a small amount of interband coupling increases its T_c reproducing the experimentally observed behavior of the large gap. However, it is no longer possible to obtain the measured gap values and the overall trend of the calculated curves is very far from the experimental one.

Thus, even if the model can partially reproduce the observed behavior of the two gaps as a function of temperature in the case shown in Fig. 2 a), in general, the standard *s*-wave two-band Eliashberg model fails in describing the trend of the gaps in the measured temperature range, indicating that the superconducting mechanism (and its possible relationship with magnetism) is certainly more complex and has still to be understood. It is also worth mentioning that, by assuming the proposed spin-fluctuation pairing mechanism [13] in our *two-band* Eliashberg model, it would be even more difficult to describe the experimental results. This kind of pairing indeed implies a strong interband coupling and no (or at least very small) intraband one, thus leading, when only two bands are involved, to the presence of a single *s*-wave gap (or two *s*-wave gaps with values close to each other). By taking into account a more realistic band structure of iron pnictides made by two hole sheets and an equivalent electron one it is possible to introduce a three-band model. It has been shown in the framework of the standard BCS theory that such a three-band $s\pm$ model with only interband couplings can reproduce the experimental observation of two gaps with a ratio $\Delta_2/\Delta_1 \approx 2-3$ [27]. However this is not true in the framework of the Eliashberg model where it is necessary to introduce a certain amount of intraband coupling[1] in order to obtain such a large Δ_2/Δ_1 ratio. In any case a temperature dependence of Δ_1 like that shown in Fig. 2 a) cannot be simply reproduced within the BCS or Eliashberg scenario even if a $s\pm$ symmetry in a multiband framework is considered.

At the present stage of knowledge we don't know the reason for this anomalous behaviour but we can however notice that a similar unconventional temperature dependence of the gap has also been observed in some heavy-fermion compounds such as $CeCoIn_5$ [28]. Further theoretical and experimental studies have to be conducted on these compounds in order to clarify the mechanism that leads to the occurrence of superconductivity.

[1] *G. A. Ummarino, private communication*

4. Conclusions

In summary, we presented results of PCAR measurements in the Fe-1111 layered superconductor $LaFeAsO_{1-x}F_x$. Andreev-reflection spectra clearly indicate the presence of two order parameters, in agreement with the multiband electronic structure of this compound. An unconventional behavior of the two gaps as a function of temperature has been obtained, especially for the small one, Δ_1. A theoretical analysis performed within the two-band Eliashberg theory with generic electron-boson couplings fails in describing the experimental results, revealing that much theoretical and experimental efforts have still to be carried out in order to clarify the physics of these novel and fascinating superconductors.

Acknowledgements

We thank I. I. Mazin, L. Boeri and A. Plecenik for useful discussions. V.A.S. acknowledges support by the Russian Foundation for Basic Research Project No. 09-02-00205. This work was done within the PRIN project No. 2006021741.

References

[1] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008)
[2] H. Takahashi et al., Nature, 453, 376 (2008)
[3] Z. A. Ren et al., Chinese Phys. Lett. 25, 2215 (2008)
[4] Z. A. Ren et al., Mater. Res. Innov. 12, 105 (2008)
[5] Z. A. Ren et al., Europhys. Lett. 82, 57002 (2008)
[6] Z. A. Ren et al., Europhys. Lett. 83, 17002 (2008)
[7] C. de la Cruz et al., Nature 453, 899 (2008)

[8] M. Rotter, M. Tegel, D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008)
[9] K. Sasmal, Phys. Rev. Lett. 101, 107007 (2008)
[10] F. C. Hsu et al., arXiv:0807.2369v2
[11] Y. Mizuguchi et al., Appl. Phys. Lett. 93, 152505 (2008)
[12] L. Boeri, O. V. Dolgov, A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008)
[13] I. I. Mazin, D. J. Singh, M. D. Johannes, M. H. Du, Phys. Rev. Lett. 101, 057003 (2008)
[14] G. F. Chen et al., Phys. Rev. Lett. 101, 057007 (2008)
[15] R. S. Gonnelli et al., Phys. Rev. Lett. 89, 247004 (2002)
[16] R. S. Gonnelli et al., Phys. Rev. Lett. 100, 207004 (2008)
[17] A. F. Andreev, Zh. Eksp. Teor. Fiz. 46, 1823 (1964)
[18] Goutam Sheet, S. Mukhopadhyay, P. Raychaudhuri, Phys. Rev. B 69, 134507 (2004)
[19] G. E. Blonder, M. Tinkham, T. M. Klapwijk, Phys. Rev. B 25, 4515 (1982)
[20] A. Plecenik, M. Grajcar, Š. Beňačka, P. Seidel, A. Pfuch, Phys. Rev. B 49, 10016 (1994)
[21] T. Y. Chen, Z. Tesanovic, R. H. Liu, X. H. Chen, C. L. Chien, Nature 453, 1224 (2008)
[22] S. Kashiwaya, Y. Tanaka, M. Koyanagi, K. Kajimura, Phys. Rev. B 53, 2667 (1996)
[23] W. Lu et al., Solid State Commun. 148, 168 (2008)
[24] R. S. Gonnelli et al., arXiv:0807.3149v1
[25] H. Suhl, B. T. Matthias, L. R. Walker, Phys. Rev. Lett. 3, 552 (1959)
[26] E. J. Nicol, J. P. Carbotte, Phys. Rev. B 71, 054501 (2005)
[27] L. Benfatto, M. Capone, S. Caprara, C. Castellani, C. Di Castro, Phys. Rev. B 78, 140502(R) (2008)
[28] W. K. Park, L. H. Green, J. L. Sarrao, J. D. Thompson, Phys. Rev. B 72, 052509 (2005)