

## Superconducting Energy Gap and $c$ -Axis Plasma Frequency of (Nd, Sm)FeAsO<sub>0.82</sub>F<sub>0.18</sub> Superconductors from Infrared Ellipsometry

A. Dubroka,<sup>1</sup> K. W. Kim,<sup>1</sup> M. Rössle,<sup>1</sup> V. K. Malik,<sup>1</sup> A. J. Drew,<sup>1</sup> R. H. Liu,<sup>2</sup> G. Wu,<sup>2</sup> X. H. Chen,<sup>2</sup> and C. Bernhard<sup>1,\*</sup>

<sup>1</sup>*Department of Physics and Fribourg Center for Nanomaterials, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland*

<sup>2</sup>*Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*

(Received 15 May 2008; published 29 August 2008)

We present far-infrared ellipsometric measurements of polycrystalline samples of the pnictide superconductor RFeAsO<sub>0.82</sub>F<sub>0.18</sub> ( $R = \text{Nd}$  and  $\text{Sm}$ ). We find evidence that the electronic properties are strongly anisotropic such that the optical spectra are dominated by the weakly conducting  $c$ -axis response similar to the cuprate high-temperature superconductors. We deduce an upper limit of the  $c$ -axis superconducting plasma frequency of  $\omega_{\text{pl},c}^{\text{SC}} \leq 260 \text{ cm}^{-1}$  corresponding to a lower limit of the  $c$ -axis magnetic penetration depth of  $\lambda_c \geq 6 \mu\text{m}$  and  $\lambda_c/\lambda_{ab} \geq 30$  as compared to  $\lambda_{ab} = 185 \text{ nm}$  from muon spin rotation [A. Drew *et al.*, arXiv:0805.1042 [Phys. Rev. Lett. (to be published)]]. We also observe a gaplike suppression of the conductivity in the superconducting state with a shoulderlike feature at  $\omega_{\text{SC}}^* \approx 300 \text{ cm}^{-1}$  and spectral shape which is consistent with an unconventional order parameter with  $2\Delta \approx \omega_{\text{SC}}^* \approx 37 \text{ meV}$ .

DOI: 10.1103/PhysRevLett.101.097011

PACS numbers: 74.70.-b, 74.25.Gz, 78.30.-j

The recent observation of superconductivity (SC) with critical temperatures  $T_c$  up to 55 K in the layered tetragonal pnictide RFeAsO<sub>1-x</sub>F<sub>x</sub> with  $R = \text{La}, \text{Nd}, \text{Pr}, \text{Gd},$  and  $\text{Sm}$  marks the first discovery of a non-copper-oxide-based layered high- $T_c$  superconductor (HTSC) [1–3]. It raises the question of whether a common pairing mechanism is responsible for HTSC in both the cuprates and the pnictides. Similar to cuprates, the pnictides have a layered structure that is comprised of alternating FeAs and LaO sheets with Fe arranged on a square lattice [1]. Theoretical calculations predict a quasi-two-dimensional electronic structure with metallic FeAs layers and LaO layers that mainly act as blocking layers and as charge reservoir upon chemical substitution [4–6]. Also in analogy to the cuprates, SC emerges upon doping away from a magnetic parent compound [7,8], the maximal  $T_c$  occurring just as magnetism disappears [9]. There are also some clear differences with respect to the cuprates. Band structure calculations suggest that the pnictides are multiband superconductors with up to five FeAs-related bands crossing the Fermi level [4–6,10] as opposed to the cuprates which, due to a strong Jahn-Teller distortion, have only one relevant Cu( $3d_{x^2-y^2}$ )O band. Furthermore, in these pnictides the highest  $T_c$  values are achieved upon electron doping [11].

Further progress in assessing the differences and similarities of these cuprate and pnictide superconductors requires experimental information especially about their electromagnetic properties. The research into the cuprate HTSC has shown that infrared spectroscopy can play an important role since it provides fairly direct and reliable information about the electronic properties in the normal state as well as in the SC state [12,13]. Even measurements on polycrystalline samples yielded first important information. In particular, it was established that thanks to

the very large electronic anisotropy of the cuprates, the pronounced features of the reflectivity spectra are representative of the weakly conducting  $c$ -axis response [12–18]. Accordingly, from polycrystals one can obtain valuable information on the eigenfrequency of the  $c$ -axis phonon modes, the upper limit of the  $c$ -axis plasma frequency of the SC condensate,  $\omega_{\text{pl}}^{\text{SC}}$ , and the magnitude of the SC energy gap,  $\Delta$ .

Concerning the optical properties of the pnictides, so far only few reports have been reported on the undoped mother compound [19] and superconducting LaO<sub>0.9</sub>F<sub>0.1</sub>FeAs [20,21] which did not detail the impact of SC on the dielectric function. In this Letter we provide such information based on ellipsometric measurements of the far-infrared dielectric response of polycrystalline samples of RFeAsO<sub>0.82</sub>F<sub>0.18</sub> with  $R = \text{Nd}$  and  $\text{Sm}$  and  $T_c = 52$  and 45 K, respectively.

Polycrystalline samples with nominal composition NdFeAsO<sub>0.82</sub>F<sub>0.18</sub> ( $\text{Nd}, x = 0.18$ ) and SmFeAsO<sub>0.82</sub>F<sub>0.18</sub> ( $\text{Sm}, x = 0.18$ ) have been synthesized by conventional solid state reaction methods as described in Refs. [2,9]. Standard powder x-ray diffraction patterns were measured where all peaks could be indexed to the tetragonal ZrCuSiAs-type structure. The dc resistivity (see Fig. 1) and magnetization measurements were made to determine the midpoint (10%–90% width) of the resistive and diamagnetic transitions  $T_c$  ( $\Delta T_c$ ) of 52(3) K for Nd,  $x = 0.18$  of 45(3) for Sm,  $x = 0.18$ . The samples were polished using diamond suspension to obtain flat and shiny surfaces. While these were somewhat porous, our ellipsometry measurements showed that these did not give rise to strong depolarization effects.

The infrared ellipsometry measurements in the range 45–640  $\text{cm}^{-1}$  (5–80 meV) were performed with a home-

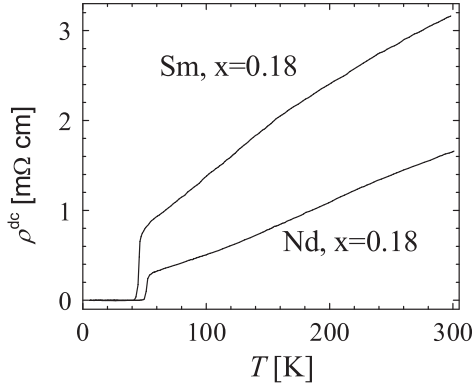


FIG. 1. Temperature dependent resistivity of the polycrystalline  $\text{NdFeAsO}_{0.82}\text{F}_{0.18}$  and  $\text{SmFeAsO}_{0.82}\text{F}_{0.18}$  samples.

built setup attached to a Bruker 113V fast-Fourier spectrometer as described in Ref. [22]. The angle of incidence of the polarized light was  $80^\circ$ . Ellipsometry enables one to directly measure the complex dielectric function,  $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ , and the related optical conductivity  $\tilde{\sigma}(\omega) = -i\omega\epsilon_0[\tilde{\epsilon}(\omega) - 1]$ , without a need for Kramers-Kronig analysis [23]. Furthermore, it is a self-normalizing technique that enables very accurate and reproducible measurements.

Figure 2 displays the infrared optical spectra of the Nd,  $x = 0.18$  sample at representative temperatures between 10 and 300 K. Figure 2(a) shows the real part of the optical conductivity,  $\sigma_1(\omega)$ , and Fig. 2(c) the corresponding real part of the dielectric function,  $\epsilon_1(\omega)$ , while Figs. 2(b) and 2(d) detail the SC-induced changes. The inset of Fig. 2(a) shows the calculated reflectivity spectra which agree well with previously reported ones [19,21]. It is immediately evident from our data that the electronic part of the optical response is extremely weak. The most pronounced features are indeed due to the infrared-active phonon modes which give rise to narrow peaks near 102, 257, 270, and 440  $\text{cm}^{-1}$ . The electronic part of  $\sigma_1(\omega)$  has a surprisingly small magnitude of less than 100  $\Omega^{-1}\text{cm}^{-1}$  and there is only a very weak signature of an inductive response in  $\epsilon_1(\omega)$  which becomes negative only below 300  $\text{cm}^{-1}$ . We obtained very similar optical data on four additional samples which contained Sm and La instead of Nd.

This weakly conducting behavior needs to be reconciled with the metallic dc transport with  $\rho^{\text{dc}} = 0.35 \text{ m}\Omega \text{ cm}$  and  $\sigma^{\text{dc}} = 2800 \Omega^{-1}\text{cm}^{-1}$  at 60 K (the Nd,  $x = 0.18$  sample) and also with the short in-plane magnetic penetration depth of  $\lambda_{ab} = 185\text{--}235 \text{ nm}$  and thus sizable SC plasma frequency of  $\omega_{\text{pl},ab}^{\text{SC}} \approx 6500\text{--}8500 \text{ cm}^{-1}$  as obtained from muon spin rotation (in parts on the same samples) [24,25].

An explanation of this puzzling behavior can be found in the literature on the earlier infrared studies on polycrystalline samples of the cuprate HTSC and their comparison to later measurements on the  $c$ -axis response of single crystals [14–18]. Very similar trends were observed here, that

are meanwhile well understood in terms of the very strong electronic anisotropy of the electronic transport parallel and perpendicular to the conducting  $\text{CuO}_2$  planes. The pronounced features of the reflectivity spectra are representative here of the weakly conducting  $c$ -axis response. The metallic  $ab$ -plane component mostly gives rise to a moderate increase of the overall magnitude of the conductivity with respect to the  $c$ -axis component [12–18]. Accordingly, these previous measurements established that from polycrystals of strongly anisotropic superconductors one can obtain valuable information on the eigenfrequency of the  $c$ -axis phonon modes, the upper limit of the  $c$ -axis plasma frequency of the SC condensate,  $\omega_{\text{pl}}^{\text{SC}}$ , and the magnitude of the SC energy gap  $\Delta$ .

This can be understood for the following reasons. Since the wavelength of the infrared light,  $\lambda = 20\text{--}200 \mu\text{m}$ , exceeds the typical grain size  $d$  of about  $5\text{--}10 \mu\text{m}$ , one may think that effective medium approximations like the Bruggeman formula [26] should be applied. This is however not the case here since the optical penetration depth and thus the screening length of the dynamical depolarization fields due to the charge accumulation at the grain boundaries is less than  $1 \mu\text{m}$  and thus significantly shorter than  $d$  (see Ref. [26], p. 81). In good approximation, these depolarization fields can thus be neglected and the reflected light wave can be considered as a coherent superposition of the reflections from several individual grains (since  $\lambda > d$ ). This corresponds to the averaging of the complex Fresnel reflectance coefficients of the  $ab$ -plane and  $c$ -axis components. As was already pointed out in Refs. [14,27], the main features of the optical response can also be obtained by averaging the reflectivities  $R_c$  and  $R_{ab}$  as they would be measured on single crystals (if these were available). Accordingly, the response of such polycrystalline samples is largely dominated by the weakly conducting  $c$ -axis component where the phonons, the SC gap, and the SC plasma frequency give rise to pronounced features in  $R_c$  (as compared to  $R_{ab}$  where these features are much weaker). In the following we apply this approach to the pnictide superconductors.

Figure 2(a) shows that we observe a clear SC-induced gaplike suppression of  $\sigma_1(\omega)$ . This is detailed in Fig. 2(b) in terms of the difference spectrum between 55 and 10 K which reveals a clear shoulderlike feature at  $\omega_{\text{SC}}^* \approx 300 \text{ cm}^{-1}$  and in the inset which depicts the temperature dependence of the spectral weight between 50 and  $300 \text{ cm}^{-1}$ . Apart from a resonancelike feature between  $50\text{--}150 \text{ cm}^{-1}$  that is caused by a phonon anomaly (as discussed below), it appears that the gaplike suppression has a similar shape as in the  $c$ -axis response of the cuprate HTSC where it has been shown that  $\omega_{\text{SC}}^* \approx 2\Delta$  [13,28–30]. This relationship is valid under the conditions of a diffuse transmission and an unconventional order parameter that exhibits a sign change in  $k$  space [28,29]. These conditions seem to be fulfilled for the present pnictide superconductors.

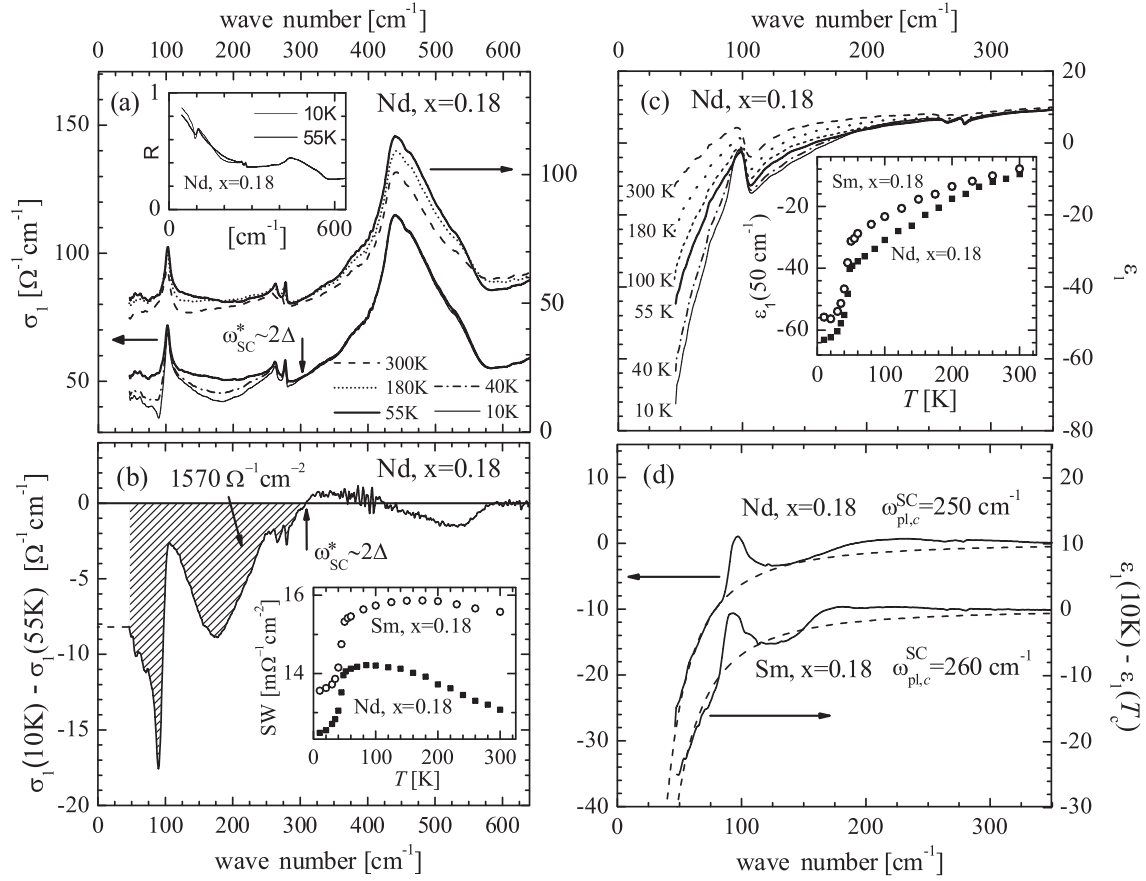


FIG. 2. Temperature dependence of the infrared dielectric response of the  $\text{NdFeAsO}_{0.82}\text{F}_{0.18}$  ( $\text{Nd}, x = 0.18$ ) and  $\text{SmFeAsO}_{0.82}\text{F}_{0.18}$  ( $\text{Sm}, x = 0.18$ ) superconductors. (a) Representative spectra of the real part of the conductivity  $\sigma_1(\omega)$  of the  $\text{Nd}, x = 0.18$  sample. The arrow marks the onset of the SC-induced gaplike suppression. The inset shows calculated reflectivity spectra. (b) Difference between the conductivity in the normal and the SC state in terms of  $\sigma_1(10\text{ K}) - \sigma_1(55\text{ K})$ . The shaded area indicates the missing spectral weight due to the SC condensate. The inset details the temperature dependence of the integral of  $\sigma_1(\omega)$  between  $45$  and  $300\text{ cm}^{-1}$  (SW). (c) Corresponding spectra of the real part of the dielectric function  $\epsilon_1(\omega)$ . The inset details the temperature evolution of  $\epsilon_1(50\text{ cm}^{-1})$ . (d) Difference spectra  $\epsilon_1(10\text{ K}) - \epsilon_1(T_c)$  (solid lines) showing the SC-induced change of  $\epsilon_1(\omega)$ . Dotted lines show fits with the function  $-(\omega_{\text{pl},c}^{\text{SC}}/\omega)^2$ .

tors. Our data suggest indeed that the  $c$ -axis response is barely metallic and an unconventional order parameter symmetry is compatible with recent NMR [31,32] and angle resolved photoemission spectroscopy measurements [33] as well as with the spectral shape of the SC-induced suppression of  $\sigma_1(\omega)$  which remains incomplete even at the lowest measured frequencies. Under these assumptions we thus derive  $2\Delta \approx \omega_{\text{SC}}^* \approx 37\text{ meV}$  and a ratio of  $2\Delta/k_B T_c \approx 8$  that is suggestive of strong-coupling superconductivity. We note that a smaller gap value would result for the case of an isotropic order parameter [34] or an anisotropic one without a sign change in  $k$  space [29]. We also note that the pnictides may well be multiband superconductors with several SC energy gaps where our estimate would refer to the largest gap value.

As mentioned above, our data reveal an anomalous temperature dependence of the phonon mode near  $100\text{ cm}^{-1}$  which exhibits an asymmetric shape below  $T_c$  [see Figs. 2 (a) and 2(b)]. This shape change causes the wavy structure

in the conductivity difference spectrum in Fig. 2(b). Such behavior might be taken as evidence that this phonon mode strongly couples to the electronic background. However, it appears that the peak frequency of the phonon mode does not exhibit any corresponding change. Furthermore, we remark that similar anomalous shapes of phonon modes were previously observed on polycrystalline cuprate HTSC samples [16] that were not confirmed by subsequent measurements on single crystals [13].

Under the assumption of the prevalence of the  $c$ -axis component in the optical response of our polycrystalline samples, we can also deduce another important parameter of the SC state which is the upper limit of the  $c$ -axis plasma frequency of the SC condensate  $\omega_{\text{pl},c}^{\text{SC}}$  or the related magnetic penetration depth  $\lambda_c$ . These values can be derived from our data in two independent ways [since ellipsometry measures  $\sigma_1(\omega)$  and  $\epsilon_1(\omega)$  independently]. First, one can obtain them from the so-called missing area due to the gaplike suppression in the regular part of  $\sigma_1(\omega)$ . As shown

in Fig. 2(b) by the shaded area for the measured frequency range of 45–300  $\text{cm}^{-1}$ , this amounts to 1570  $\Omega^{-1} \text{cm}^{-2}$  or  $\omega_{\text{pl},c}^{\text{SC}} = 245 \text{ cm}^{-1}$ . These values are likely even somewhat larger due to a contribution from the frequency range below 45  $\text{cm}^{-1}$ . As an example, the dotted line shows a straight extrapolation which would yield a value of 1940  $\Omega^{-1} \text{cm}^{-2}$  or  $\omega_{\text{pl},c}^{\text{SC}} = 270 \text{ cm}^{-1}$ . Second, the plasma frequency of the SC condensate can be determined from the inductive response in  $\epsilon_1(\omega)$  where a SC-induced contribution is apparent in the temperature evolution of  $\epsilon(50 \text{ cm}^{-1})$ ; see the inset of Fig. 2(c). As shown in Fig. 2(d), reasonable fits to the low frequency parts of the difference spectra of  $\epsilon_1(\omega)$  between the 10 K and the temperature right above  $T_c$  can be obtained with the function,  $-(\omega_{\text{pl},c}^{\text{SC}}/\omega)^2$ , that accounts for the inductive response due to the SC condensate. For both samples we obtained a similar value of  $\omega_{\text{pl},c}^{\text{SC}} = 250\text{--}260 \text{ cm}^{-1}$  which translates into a spectral weight of the SC condensate of  $\approx 1700 \Omega^{-1} \text{cm}^{-2}$ . We note that the determination of  $\omega_{\text{pl},c}^{\text{SC}}$  in both cases is based on the assumption that the regular part of the dielectric function does not change between 10 and 55 K. Because of a possible narrowing of the regular part below  $T_c$ , our analysis may well give a slightly overestimated value of  $\omega_{\text{pl},c}^{\text{SC}}$  which nevertheless provides a reliable upper boundary. Accordingly, we can derive from our data a lower limit of the magnetic penetration depth in the  $c$ -axis direction of  $\lambda_c \geq 6 \mu\text{m}$ . With the in-plane values of  $\lambda_{ab} \approx 185\text{--}235 \text{ nm}$  as obtained from recent muon-spin-rotation measurements (that were in parts performed on the same samples) [24,25] this yields an anisotropy of  $\lambda_c/\lambda_{ab} \geq 30$ . Once more we note that rather similar values have been obtained, for example, for weakly underdoped to optimally doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  single crystals [35].

In summary, we reported infrared optical measurements of polycrystalline samples of the  $(\text{Nd, Sm})\text{FeAsO}_{0.82}\text{F}_{0.18}$  superconductors which reveal several similarities with the cuprate high-temperature superconductors. Our optical spectra provide evidence for a strong electronic anisotropy such that the weakly conducting  $c$ -axis response prevails in the optical response of our polycrystalline samples. Under this assumption we can deduce important parameters like a lower limit for the  $c$ -axis magnetic penetration of  $\lambda_c \geq 6 \mu\text{m}$  and an anisotropy of  $\lambda_c/\lambda_{ab} \geq 30$  compared to  $\lambda_{ab} = 185 \text{ nm}$  from muon spin rotation [25]. Our data also reveal a clear SC-induced gaplike suppression of the conductivity with a shoulderlike feature around 300  $\text{cm}^{-1}$  and an overall spectral shape that can be interpreted in terms of an unconventional order parameter of magnitude  $2\Delta \approx \omega_{\text{SC}}^* \approx 37 \text{ meV}$ .

We acknowledge helpful discussion with D. Munzar and J. Humlíček. This work is supported by the Schweizer Nationalfonds (SNF) with Grant 200020-119784, the NCCR Materials with Novel Electronic Properties-

MaNEP, and by the Deutsche Forschungsgemeinschaft (DFG) with Grant BE2684/1-3 in FOR538.

\*Christian.Bernhard@unifr.ch

- [1] Y. Kamihara *et al.*, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [2] X. H. Chen *et al.*, *Nature (London)* **453**, 761 (2008).
- [3] Z. A. Ren *et al.*, *Chin. Phys. Lett.* **25**, 2215 (2008).
- [4] S. Lebegue, *Phys. Rev. B* **75**, 035110 (2007).
- [5] D. J. Singh and M. H. Du, *Phys. Rev. Lett.* **100**, 237003 (2008).
- [6] K. Haule, J. H. Shim, and G. Kotliar, *Phys. Rev. Lett.* **100**, 226402 (2008).
- [7] Clarina de la Cruz *et al.*, *Nature (London)* **453**, 899 (2008).
- [8] H.-H. Klauss *et al.*, *Phys. Rev. Lett.* **101**, 077005 (2008).
- [9] R. H. Liu *et al.*, arXiv:0804.2105.
- [10] Gang Xu *et al.*, *Europhys. Lett.* **82**, 67002 (2008).
- [11] Hai-Hu Wen *et al.*, *Europhys. Lett.* **82**, 17009 (2008).
- [12] D. B. Tanner and T. Timusk, in *Physical Properties of High Temperature Superconductors II*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), p. 363.
- [13] D. N. Basov and T. Timusk, *Rev. Mod. Phys.* **77**, 721 (2005).
- [14] Z. Schlesinger, R. T. Collins, M. W. Shafer, and E. M. Engler, *Phys. Rev. B* **36**, 5275 (1987).
- [15] D. A. Bonn *et al.*, *Phys. Rev. B* **35**, 8843 (1987).
- [16] D. A. Bonn *et al.*, *Phys. Rev. Lett.* **58**, 2249 (1987).
- [17] C. C. Homes, T. Timusk, R. Liang, D. A. Bonn, and W. N. Hardy, *Phys. Rev. Lett.* **71**, 1645 (1993).
- [18] S. Uchida, K. Tamasaku, and S. Tajima, *Phys. Rev. B* **53**, 14558 (1996).
- [19] G. F. Chen *et al.*, *Phys. Rev. Lett.* **100**, 247002 (2008).
- [20] G. F. Chen *et al.*, *Phys. Rev. Lett.* **101**, 057007 (2008).
- [21] S. Drechsler *et al.*, arXiv:0805.1321.
- [22] C. Bernhard, J. Humlíček, and B. Keimer, *Thin Solid Films* **455–456**, 143 (2004).
- [23] R. M. A. Azzam and N. H. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).
- [24] H. Luetkens *et al.*, arXiv:0804.3115 [*Phys. Rev. Lett.* (to be published)].
- [25] A. Drew *et al.*, arXiv:0805.1042 [*Phys. Rev. Lett.* (to be published)].
- [26] A. Sihvola, *Electromagnetic Mixing Formulas and Applications* (Institution of Electrical Engineers, London, 1999).
- [27] T. G. Mayerhöfer, Z. Shen, R. Keding, and J. L. Musfeldt, *Phys. Rev. B* **71**, 184116 (2005).
- [28] P. J. Hirschfeld, S. M. Quinlan, and D. J. Scalapino, *Phys. Rev. B* **55**, 12742 (1997).
- [29] M. Palumbo and M. J. Graf, *Phys. Rev. B* **53**, 2261 (1996).
- [30] L. Yu *et al.*, *Phys. Rev. Lett.* **100**, 177004 (2008).
- [31] Y. Nakai *et al.*, arXiv:0804.4765.
- [32] K. Ahilan *et al.*, arXiv:0804.4026.
- [33] C. Liu *et al.*, arXiv:0806.2147.
- [34] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).
- [35] T. Shibauchi *et al.*, *Phys. Rev. Lett.* **72**, 2263 (1994).