Substitution of Sc for Mg in MgB_2: Effects on transition temperature and Kohn anomaly

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Here we report the synthesis and characterization of $Mg_{1-x}Sc_xB_2$ $(0.12<x<0.27)$ system, with critical temperature in the range of $30>T_c>6$ K. We find that the Sc doping moves the chemical potential through the 2-D/3-D electronic topological transition (ETT) in the σ band where the "shape resonance" of interband pairing occurs. In the 3-D regime beyond the ETT we observe a hardening of the E_{2g} Raman mode with a significant line-width narrowing due to the suppression of the Kohn anomaly over the range $0<q<2k_F$.

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Following the discovery of superconductivity in MgB_2 with a T_c of 40 K[1] large attention has been paid to chemical substitutions[2–8] aiming at the enhancement of T_c and H_{c2}, and to manipulate the electronic structure for the understanding of the high T_c superconductivity. As a matter of fact, chemical substitution in MgB_2 is difficult and only Al replacing Mg[4–7] and C replacing B[8] had been successful. Both of these substitutions reduce the T_c and induce a lattice compression. The variation of T_c with doping is mostly determined by the tuning of the chemical potential through the electronic topological transition (ETT) where the topology of the Fermi surface of the σ band changes from 2D to 3D.[6] In this two-gap superconductor[9] the exchange-like nondiagonal σ-π interband pairing terms that enhance T_c are expected to exhibit large variation near the ETT.[5,6] In addition, Raman spectroscopy measurements on the $Mg_{1-x}Al_xB_2$ and $MgB_{2-x}C_x$ systems[10–13] have revealed a line-width narrowing and energy hardening of the E_{2g}-mode with the substitution beyond the ETT. This effect could be interpreted in terms of suppression of the Kohn anomaly[14,15] observed over an extended range $0<q<2k_F$ in MgB_2[16,17] by a shift of the Fermi level. In fact the Kohn anomaly[18] is strong (weak) for a 2-D (3-D) Fermi surface.[19,20] Therefore it is expected to decrease for a 2-D to 3-D ETT[6,21] of the Fermi surface. The proximity to an ETT has been invoked to explain the anomalous pressure dependence[22] of this mode and it has been proposed to be the driving mechanism for raising the critical temperature.[6,23,24] Our aim in this work is to modify the band structure by chemical substitutions to explore the role of electronic structure in the MgB_2 on the electron-phonon coupling and on T_c by tuning the chemical potential through the shape resonance.

We have synthesized the new superconducting ternary system $Mg_{1-x}Sc_xB_2$ for $0.12<x<0.27$, where the chemical substitution induces minor lattice variations since the ionic radius of Sc (1.62 Å) is only a little larger than of Mg (1.602 Å). The substituted Sc ions donate $0.12<x<0.27$ electrons per unit cell to the conduction σ and π bands so the chemical potential is shifted towards the top of the σ band beyond the ETT[6] where the σ Fermi surface changes from a 2-D to a 3-D topology, expected near $x=0.12$.[9,18] Sc substitution for Mg increases the disorder in the Mg/Sc layers but has minor effects on the lattice structure of the boron layer. Therefore the variation of T_c and electron–phonon coupling with the variation of the electron structure can be well investigated.

In these new samples we observe a remarkable line narrowing and frequency hardening of the E_{2g} Raman mode, which gives compelling experimental evidence for a drastic reduction of the Kohn anomaly and of the electron phonon coupling for $x>0.12$. It is remarkable to note that the critical temperature in the $Mg_{1-x}Sc_xB_2$ samples has been dropped only by a factor 2–10 from MgB_2, much less than expected for a multi-band theory (with doping-independent interband pairing) considering the decrease of the electron-phonon coupling and of the density of states in the σ band. This suggests importance of the resonant enhancement of the interband pairing term[23] and the associated minimum of the nondiagonal Coulomb pseudo-potential[24] that drives the T_c amplification at the ETT, called "shape resonance" in a two-gap superconductor.

$Mg_{1-x}Sc_xB_2$ samples were synthesized by a direct reaction method of elemental magnesium and scandium (powder, 99.9 mass % nominal purity), boron (99.5% pure <60 mesh powder). The starting materials were mixed in a stoichio-

metric ratio and pressed into pellets of 8 mm in diameter. Each pellet was enclosed in a tantalum crucible and sealed by arc welding under an argon atmosphere. The Ta crucibles were then heated in a furnace Centorr M60 under a high-pure Ar atmosphere for 14 hours in the temperature range between 1280 and 950 °C.

The phase purity of the samples was checked by x-ray diffraction. The diffraction patterns of $Mg_{1-x}Sc_xB_2$ samples were measured in the Bragg-Brentano θ-θ geometry by a vertical X'Pert Pro MPD diffractometer using a Cu K_α radiation. The x-ray diffraction measurements of several samples were repeated at the beamline ID31 of the European Synchrotron Radiation Facility (ESRF), Grenoble. The samples were sealed in 1.0 mm diameter glass capillaries and the high-resolution diffraction profiles ($\lambda = 0.5$ Å) were collected at $T = 80$ K using nine Ge(111) analyzer crystals. The reflections were indexed to a MgB_2-like structure according to the hexagonal AlB_2 structure type (P6/mmm space group). No Sc, Sc_2O_3 or ScB_{12} minority phases were found, which indicates a successful Sc substitution for Mg. Figure 1(a) shows profiles of (002) and (110) diffraction peaks for a representative sample of the $Mg_{1-x}Sc_xB_2$ system. A line broadening is observed in Sc-doped compounds as compared to MgB_2 and ScB_2 indicating disorder or nonuniformities due to Mg/Sc layers.

The samples were characterized for their superconducting properties by the temperature dependence of complex conductivity using the single-coil inductance method.[5,6] The temperature dependent radio-frequency complex conductivity for representative Sc contents is shown in Fig. 1(b) where it can be seen that the introduction of Sc in the Mg-planes induces a clear shift of the superconducting transition to lower temperatures. The superconducting transition for the Sc-doped samples shows a broadening. This indicates that some disorder does exist in the Sc-doped samples with a possible effect on the superconductivity via an increase of intraband scattering in the π band.

The Raman spectra were measured in the back-scattering geometry, using a T64000 Jobin-Yvon triple spectrometer with a charge-coupled device camera. The explored Raman shift ranges between 200 and 1100 cm^{-1}. The 488.0 nm Ar^+ laser line was focused on $1-2$ μm large crystallites and the power was kept below 0.03 mW to avoid heating by the beam. Typical spectra recorded for selected temperatures are shown in Fig. 1(c). The in-plane boron vibration with E_{2g} symmetry produces a single narrow peak in the Raman spectrum of ScB_2 as in AlB_2[10,12] also if at lower energy according with its larger lattice parameters. The Raman line is softened going from ScB_2 to $Mg_{1-x}Sc_xB_2$ and finally becomes very soft and very broad in MgB_2.

The diffraction data were analyzed by Rietveld refinement using the GSAS program. The behavior of the lattice parameters *a* and *c* as a function of Sc content is reported in Fig. 2. A miscibility gap occurs in the range from $2 \pm 1\%$1% to $12 \pm 1\%$ Sc substitution where the samples show a macroscopic phase separation between low-doped and high-doped samples. The *a*-axis increases gradually with increasing Sc-content, while the *c*-axis is nearly constant. The unit cell volume shows a small expansion in agreement with the similar ionic radius between Sc^{3+} and Mg^{2+}. For a comparison in

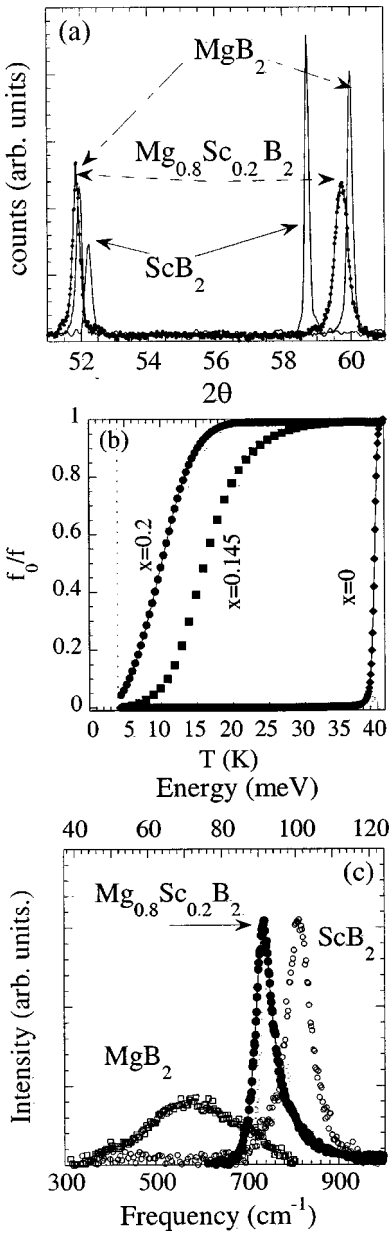

FIG. 1. The x-ray diffraction patterns in the range of the (001) and (110) reflections [panel (a)], the superconducting transition measured by complex resistivity [panel (b)], and the Raman spectra [panel (c)] are shown for representative $Mg_{1-x}Sc_xB_2$ samples compared with MgB_2 and ScB_2.

the same figure we report the evolution of the lattice parameters in the $Mg_{1-x}Al_xB_2$ system that shows much larger lattice variations. Here "*x*" is the nominal Sc-content and we can conclude that the introduced Sc is successfully substituted for Mg, and the actual Sc-content is not much different from the nominal value. From the variation of lattice parameters with a Sc content, we can conclude that the solubility range of scandium in MgB_2 is between 12% and 27%.

The variation of the superconducting critical temperature T_c as a function of Sc doping is reported in panel (a) of Fig. 3. The transition temperature T_c was determined from the peak in the derivative of the complex conductivity. The T_c decreases continuously with increasing Sc substitution from

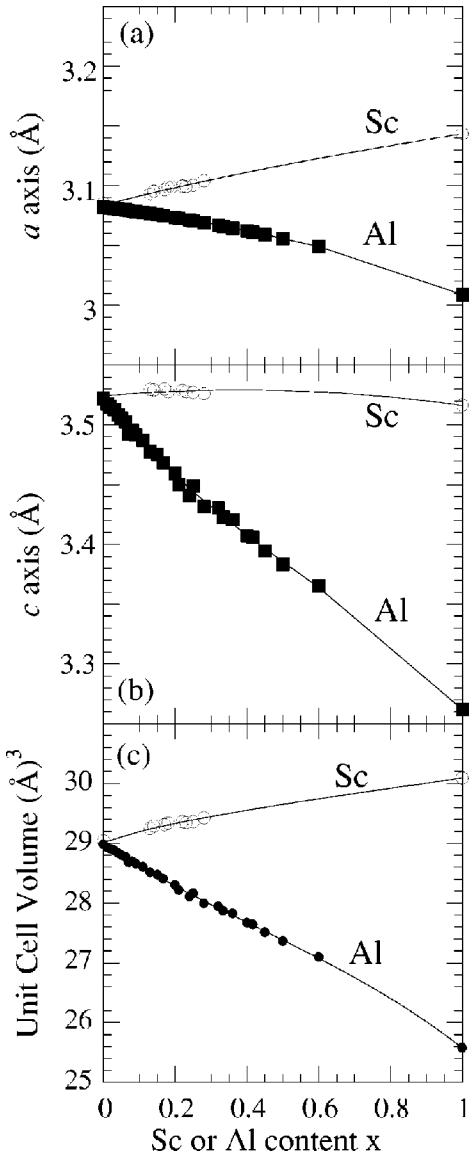

FIG. 2. Changes of lattice parameters a [panel (a)] and c [panel (b)] and of unit cell volume [panel (c)] as a function of Sc content x in $Mg_{1-x}Sc_xB_2$.

30 K at 12% to 6 K at 27%. It is interesting to note that the variation of $T_c(x)$ is sharper for $0.12<x<0.15$.

Panel (b) of Fig. 3 shows the variation of the frequency of the E_{2g} Raman line from MgB_2 to $Mg_{1-x}Sc_xB_2$. The error bars indicate the E_{2g} peak half-width. In the Sc-substituted samples in the range 12%–27% the phonon peak is shifted toward higher frequency; it is much narrower in comparison with MgB_2 and it is approaching frequency of that for the ScB_2. The frequency hardening and the line-width narrowing of the Raman E_{2g} mode indicates a clear decrease of the electron–phonon coupling going from MgB_2 to the Sc-doped samples.

Finally in Fig. 4 we report the energy of the Raman E_{2g} mode as a function of the a-axis (that is the relevant parameter for the in plane high frequency longitudinal optical mode E_{2g}) of the nonsuperconducting diborides ScB_2 and AlB_2, and of the superconducting MgB_2, $Mg_{1-x}Sc_xB_2$ and $Mg_{0.5}Al_{0.5}B_2$[13] systems.

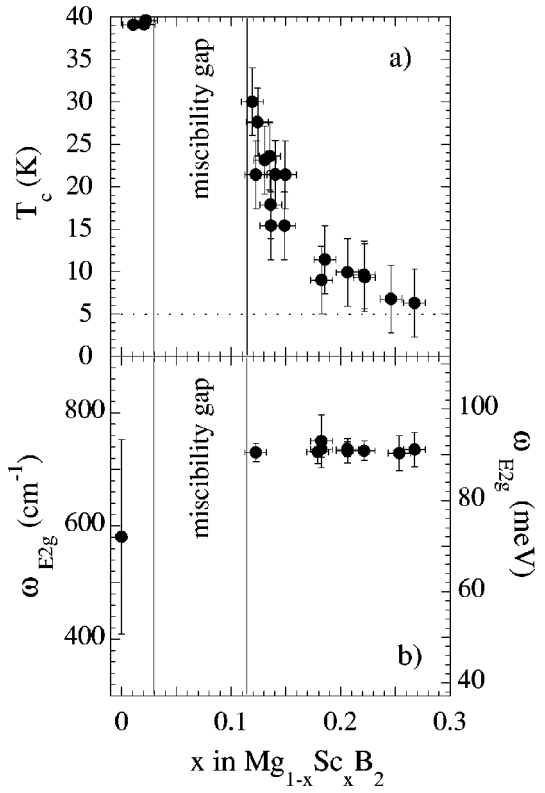

FIG. 3. Evolution of the superconducting critical temperature T_c [panel (a)], the frequency $\omega_{E_{2g}}$ [panel (b)] of the E_{2g} Raman line as a function of x in $Mg_{1-x}Sc_xB_2$. The superconductive transition width and the E_{2g} peak half-width are indicated as error bars, respectively, in panel (a) and panel (b).

Let us consider first the AlB_2 and ScB_2 samples with a filled σ band. The energy of the E_{2g} mode as a function of the a-axis follows the law $\Omega(a)=\omega_{Al}(a/a_{Al})^{-3\gamma_{0a}}$ [a dashed line in panel (a)] where γ_{0a} is the Gruneisen parameter $\gamma_{0a}=-\partial \ln \nu/3\partial \ln a=1.4\pm0.1$ that is the expected behavior due to lattice expansion for a metallic covalent material.

In the case where the Fermi level is tuned below the top of the σ band (e.g., MgB_2, $Mg_{1-x}Sc_xB_2$ and $Mg_{0.5}Al_{0.5}B_2$) a phonon decay channel opens up unlike others with a filled σ band (e.g., AlB_2 and ScB_2). In fact the phonons can now decay into electron-hole excitations in the σ band inducing a phonon energy softening and line broadening (Kohn anomaly). The E_{2g} phonon softening can be obtained by the energy difference between the experimental E_{2g} Raman energy $\omega_{E_{2g}}$ and the expected phonon energy Ω_{2g} (a) for a material with a filled σ band and with the appropriate lattice parameter. We deduce the large phonon softening of 37 meV for MgB_2 and about 17 meV for a $Mg_{1-x}Sc_xB_2$ system that is close to the case of $Mg_{0.5}Al_{0.5}B_2$. The Raman softening in MgB_2 is due to a large electron-phonon interaction with the electron-hole excitations in the σ band that drives the system close to a lattice instability and the breakdown of the Migdal approximation.[9,18] The decrease of the electron-phonon coupling near $q=0$ going from MgB_2 to $Mg_{1-x}Sc_xB_2$ is given by the variation of the ratio $[\Omega_{E_{2g}}(q=0)/\omega_{E_{2g}}(q=0)]^2$

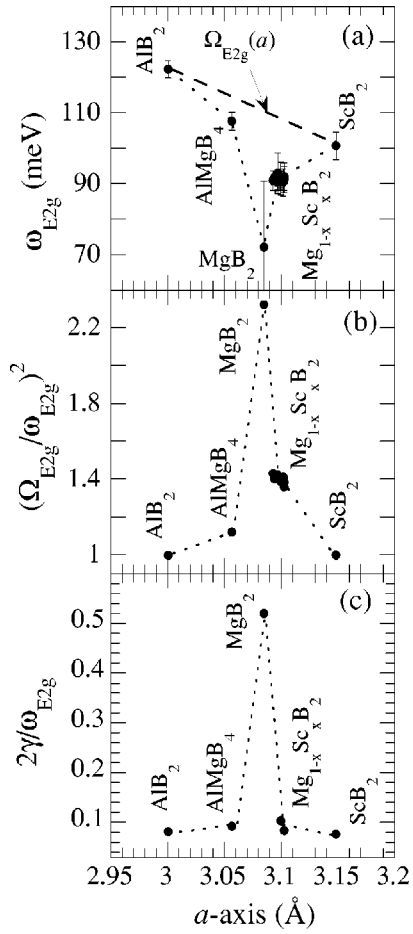

FIG. 4. Variation of the frequency of the E_{2g} Raman line as a function of the lattice parameter a for the different diborides [panel (a)]. The softening and broadening of the E_{2g} mode due to the Kohn anomaly is given by the energy ratio $(\Omega_{E_{2g}}(a)/\omega_{E_{2g}}(a))^2$ [panel (b)] and the ratio $2\gamma/\omega_{E_{2g}}$ [panel (c)] where 2γ is the Raman line width.

shown in panel (b) going from 2.2 in MgB_2 to 1.4 in $Mg_{0.8}Sc_{0.2}B_2$. This drastic decrease is related to a smaller E_{2g} Kohn anomaly in $Mg_{1-x}Sc_xB_2$. This result is confirmed by the variation of the ratio between the line-width and the phonon energy $2\gamma/\omega_{E_{2g}}$ shown in panel (c) of Fig. 4 that decreases going from MgB_2 to $Mg_{0.8}Sc_{0.2}B_2$. These results can be understood if the Sc substitution has driven the chemical potential through the ETT where the σ Fermi surface has a 3-D topology[6] with a reduced Kohn anomaly.[14,15]

In conclusion, we have reported the successful substitution of Sc for Mg with $0.12<x<0.27$ obtaining a very small lattice expansion. The system shows a miscibility gap in the range $0.2<x<0.12$, which supports the fact that the system is in the proximity of a lattice instability expected at the 2.5 Lifshitz phase transition[21] in agreement with pressure effect measurements.[22] The effect of the Sc doping is to shift the chemical potential toward the ETT and the top of the σ band. However the rigid band model is not appropriate since we expect that the Sc substitution increases the sp^2(B)-d(Sc) hybridization and the dispersion of the σ band.

In the $Mg_{1-x}Sc_xB_2$ samples the E_{2g} Raman mode shows a large hardening and narrowing in comparison with MgB_2 while the lattice expands, which indicates a drastic reduction of the Kohn anomaly in the E_{2g} longitudinal optical mode. This effect has been associated with the tuning of the Fermi level beyond the critical energy for the ETT where the two-dimensional topology of the σ Fermi surface changes to a three-dimensional topology. The critical temperature in the $Mg_{1-x}Sc_xB_2$ samples has been found in the range 30–6 K as in the case of Al substituted samples in the regime where the Fermi surface of the σ band has a 3-D topology beyond the 2-D/3-D ETT[6]. The high values of T_c in this multi-band superconductor are associated with the key role of the nondiagonal interchannel pairing term and Coulomb pseudopotential term as in the case of Al substitution.[23,24] These new data support the key role of the electronic structure controlling the resonant enhachement of the exchange-like interband coupling term in a two-gap superconductor. This occurs when the chemical potential is tuned in an energy window around the 2-D/3-D electronic topological transition in one of the two Fermi surface portions giving the shape resonance[25] that pushes up the critical temperature.

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[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).

[2] C. Buzea and T. Yamashita, Supercond. Sci. Technol. **14**, R115 (2001).

[3] R. J. Cava, H. W. Zandbergen, and K. Inumaru, Physica C **385**, 8 (2003).

[4] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. Loureiro, M. Haas, H. W. Zandbergen, and R. J. Cava, Nature (London) **410**, 343 (2001).

[5] S. Agrestini, D. Di Castro, M. Sansone, N. L. Saini, A. Saccone, S. De Negri, M. Giovannini, M. Colapietro, and A. Bianconi, J. Phys.: Condens. Matter **13**, 11689 (2001).

[6] A. Bianconi, D. Di Castro, S. Agrestini, G. Campi, N. L. Saini, A Saccone, S. De Negri, and M. Giovannini, J. Phys.: Condens. Matter **13**, 7383 (2001); A. Bianconi, D. Di Castro, S. Agrestini, G. Zangari and N. L. Saini, A. Saccone, S. De Negri, M. Giovannini G. Profeta, A. Continenza, G. Satta, S. Massidda, A. Cassetta, A. Pifferi, and M. Colapietro, Phys. Rev. B **65**, 174515 (2002).

[7] J. Q. Li, L. Li, F. M. Liu, C. Dong, J. Y. Xiang, and Z. X. Zhao,

Phys. Rev. B **66**, 012511 (2002).
[8] S. Lee, T. Masui, A. Yamamoto, H. Uchiyama, and S. Tajima, Physica C **397**, 7 (2003); S. M. Kazakov, J. Karpinski, J. Jun, P. Geiser, N. D. Zhigadlo, R. Puzniak, and A. V. Mironov, cond-mat/0304656.
[9] I. I. Mazin, and V. P. Antropov, Physica C **385**, 49 (2003).
[10] K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. **86**, 5771 (2001).
[11] P. Postorino, A. Congeduti, P. Dore, A. Nucara, A. Bianconi, D. Di Castro, S. De Negri, and A. Saccone, Phys. Rev. B **65**, 020507 (2001).
[12] B. Renker, K. B. Bohnen, R. Heid, and D. Ernst, H. Schober, M. Koza P. Adelmann, P. Schweiss, and T. Wolf, Phys. Rev. Lett. **88**, 067001 (2002).
[13] D. Di Castro, S. Agrestini, G. Campi, A. Cassetta, M. Colapietro, A. Congeduti, A. Continenza, S. De Negri, M. Giovannini, S. Massidda, M. Nardone, A. Pifferi, P. Postorino, G. Profeta, A. Saccone, N. L. Saini, G. Satta, and A. Bianconi, Europhys. Lett. **58**, 278 (2002).
[14] G. Grüner, *Density Waves in Solids* (Perseus, Cambridge, MA, 2000).
[15] M. E. Flatté, Phys. Rev. B **50**, 1190 (1994).
[16] A. Shukla, M. Calandra, M. d'Astuto, M. Lazzeri, F. Mauri, C. Bellin, M. Krisch, J. Karpinski, S. M. Kazakov, J. Jun, D. Daghero, and K. Parlinski, Phys. Rev. Lett. **90**, 095506 (2003).
[17] A. Q. R. Baron, H. Uchiyama, Y. Tanaka, S. Tsutsui, D. Ishikawa, S. Lee, R. Heid, K.-P. Bohnen, S. Tajima, and T. Ishikawa, cond-mat/0309123, 2003.
[18] W. E. Pickett, Braz. J. Phys. **33**, 695 (2003); J. M. An, S. Y. Savrasov, H. Rosner, and W. E. Pickett, Phys. Rev. B **66**, 220502(R) (2002); W. E. Pickett, J. M. An, H. Rosner, and S. Y. Savrasov, Physica C **387**, 117 (2003), and references therein.
[19] S. Tsuda, T. Yokoya, Y. Takano, H. Kito, A. Matsushita, F. Yin, J. Itoh, H. Harima, and S. Shin, Phys. Rev. Lett. **91**, 127001 (2003).
[20] A. Carrington, P. J. Meeson, J. R. Cooper, L. Balicas, N. E. Hussey, E. A. Yelland, S. Lee, A. Yamamoto, S. Tajima, S. M. Kazakov, and J. Karpinski, Phys. Rev. Lett. **91**, 037003 (2003).
[21] I. M. Lifshitz, Sov. Phys. JETP **11**, 1130 (1960).
[22] A. F. Goncharov and V. V. Struzhkin, Physica C **385**, 117 (2003).
[23] A. Bussmann-Holder and A. Bianconi, Phys. Rev. B **67**, 132509 (2003).
[24] G. A. Ummarino, R. S. Gonnelli, S. Massidda, and A. Bianconi, Physica C **407**, 121 (2004).
[25] A. Bianconi, A. Valletta, A. Perali, and N. L. Saini, Physica C **296**, 269 (1998).