PHYSICAL REVIEW B **77**, 024521 (2008)

Possible mechanism of superconductivity in $PuCoGa_5$ probed by self-irradiation damage

F. Jutier,[1,*] G. A. Ummarino,[2] J.-C. Griveau,[1] F. Wastin,[1] E. Colineau,[1] J. Rebizant,[1] N. Magnani,[1] and R. Caciuffo[1]
[1]*European Commission, Joint Research Center, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*
[2]*Dipartimento di Fisica and CNISM, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*

(Received 24 September 2007; published 24 January 2008)

Measurements of the electrical resistivity of a polycrystalline $PuCoGa_5$ sample reveal significant modifications of the superconducting properties as a function of time, due to the increase of defects and impurities resulting from self-irradiation damage. More than four years of aging were necessary to detect a deviation from linearity in the time dependence of the critical temperature. The observed behavior is understood in the framework of the Eliashberg theory, confirming the "dirty" *d*-wave character which was already suggested by nuclear magnetic resonance. We show that experimental data accumulated so far can be well reproduced by assuming a phononic mechanism for superconductivity, with reasonable values of the electron-phonon coupling and Coulomb pseudopotential. Further experiments are then required to assess the role of spin fluctuations in stabilizing the superconducting state in this compound.

DOI: 10.1103/PhysRevB.77.024521 PACS number(s): 74.62.Dh, 61.80.Jh, 74.25.Qt, 74.70.Dd

I. INTRODUCTION

Despite the intensive work carried out on $PuCoGa_5$ since the discovery of its superconducting properties,[1] several crucial points remain to be clarified, such as, for example, the possibility of a magnetic nature of the Cooper pairing mediator and the role of magnetism in determining the physical origin of the superconducting behavior in this compound.[2,3] Another open question is how the actinide electronic structure affects the physical properties; for example, $NpCoGa_5$ never becomes superconducting, although it is isostructural to $PuCoGa_5$, and the presence of the spin fluctuations with the same wave vector as those which were suggested as the mediating bosons for the latter compound has been recently proved by inelastic neutron scattering.[4] As pointed out by Curro *et al.*,[3] one main ingredient of the puzzle is the impurity scattering which, in nodal superconductors, creates excitations in the superconducting gap nodes. In general, the dependence of the superconducting ground state on the impurity scattering rate Γ may be probed quantitatively by inducing defects in a controlled way, for instance, by irradiating samples with high-energy particles.[5–7] $PuCoGa_5$ is quite unique in this respect, since defects are spontaneously produced by the α decay of the Pu nuclei. This has some advantages from the experimental point of view, since the amount of self-irradiation-induced defects in aged samples depends in a well defined way on aging time and conditions; moreover, the density of defect thus attainable is spatially homogeneous and generally higher than that obtained by conventional irradiation methods.

In this paper, we report electrical resistivity measurements on a polycrystalline $PuCoGa_5$ sample aged for almost five years. This long aging time was required to observe a decrease of the critical temperature T_c below our experimental limit of 1.8 K. Moreover, a deviation from linearity in the time dependence of T_c and of the electrical resistivity ρ has been observed, whereas previous studies over shorter periods did not allow one to test this behavior.[8] To put this finding into context, we show that the observations are consistent to what is expected from Eliashberg model for superconductivity,[9–12] and that all the most significant experimental data existing for this compound can be reproduced assuming a *phononic* mechanism with reasonable values of the electron-phonon coupling and Coulomb pseudopotential. This does not exclude a possible role of spin fluctuations, but it does show that an electron-phonon coupling model involving a minimal number of free parameters can well describe the main physical behavior of $PuCoGa_5$, provided that too simple approximations are avoided.

II. THEORETICAL MODEL

In the imaginary-axis representation, the *d*-wave one-band Eliashberg theory[13] with energy-dependent normal density of states N_m^N (Refs. 14–16) is formulated by the following equations for the gap $\Delta_n(\phi)=\Delta(i\omega_n,\phi)$ and the renormalization functions $Z_n(\phi)=Z(i\omega_n,\phi)$:

$$\omega_n Z_n(\phi) = \omega_n + \pi T \sum_m \int_0^{2\pi} \frac{d\phi'}{2\pi} \lambda_{nm}(\phi,\phi') N_m^Z(\phi') + \Gamma \frac{N_n^Z}{c^2 + (N_n^Z)^2}, \qquad (1)$$

$$Z_n(\phi)\Delta_n(\phi) = \pi T \sum_m \int_0^{2\pi} \frac{d\phi'}{2\pi} [\lambda_{nm}(\phi,\phi') - \mu^*(\phi,\phi')\vartheta(\omega_c - |\omega_m|)] N_m^{\Delta}(\phi'), \qquad (2)$$

where ϑ is the Heaviside function, ω_c is a cutoff energy for the Coulomb pseudopotential μ^*, and $N_m^{\Delta}(\phi)=N_m^N(\phi)\Delta_m(\phi)/\sqrt{\omega_m^2+\Delta_m^2(\phi)}$, $N_m^Z(\phi)=N_m^N(\phi)\omega_m/\sqrt{\omega_m^2+\Delta_m(\phi)^2}$, and N_n^Z is an angular average of $N_n^Z(\phi')$ over the Fermi surface.[10]

The parameter Γ is proportional to the concentration of defects, and c is a parameter related to the electron phase shift for scattering off an impurity.[13] The nth Matsubara frequency is defined as $i\omega_n=i\pi T(2n-1)$, and T is the temperature; $\lambda_{nm}(\phi,\phi')=\lambda(i\omega_m-i\omega_n,\phi,\phi')$ is related to the electron-phonon spectral function $\alpha^2(\Omega)F(\Omega,\phi,\phi')$ through the following equation:

$$\lambda(i\omega_m - i\omega_n, \phi, \phi') = \int_0^{+\infty} \frac{\Omega\alpha^2 F(\Omega,\phi,\phi')}{(\omega_m-\omega_n)^2+\Omega^2} d\Omega, \qquad (3)$$

where Ω is the phonon frequency. We make the usual lowest-order approximation that both the electron-phonon spectral function and the Coulomb pseudopotential contain separate s- and d-wave contributions:

$$\alpha^2 F(\Omega,\phi,\phi') = \alpha^2 F_s(\Omega) + 2\alpha^2 F_d(\Omega)\cos(2\phi)\cos(2\phi') \qquad (4)$$

and

$$\mu^*(\phi,\phi') = \mu_s^* + 2\mu_d^*(\Omega)\cos(2\phi)\cos(2\phi'). \qquad (5)$$

The normal electronic density of states of PuCoGa_5 was calculated by Opahle and Oppeneer.[17] Using the fully relativistic extension of the full-potential, local-orbital minimum-basis band-structure method, these authors show that delocalized Pu $5f_{5/2}$ states form energy bands at the Fermi level, with negligible contributions from the Ga and Co valence states. Around the Fermi energy E_F, the calculated density of states can be reproduced by the simple analytical expression

$$N^N(\omega) = \frac{1+\beta\exp(-|\omega|/\alpha)}{1+\beta}, \qquad (6)$$

where $\beta = 8/5$ and $\alpha = 15$ meV. We search for solutions of Eqs. (1) and (2) having pure d-wave symmetry for the gap function $\Delta(\omega,\phi') = \Delta_d(\omega)\sqrt{2}\cos(2\phi')$ and pure s-wave form for the renormalization function $Z(\omega,\phi') = Z_s(\omega)$; the reason for this choice is that the only solution of the homogeneous integral equation for $Z_d(\omega)$ is $Z_d(\omega) = 0$, at least for reasonable values of λ_d.[18] We assume for simplicity that $\alpha^2 F_s(\Omega) = \alpha^2 F_d(\Omega)$, $\omega_c = 96$ meV, and $c = 0$. The latter assumption corresponds to the *unitary limit* for scattering off an impurity,[13] and accounts for the strong impurity scattering already pointed out by a previous analysis of NMR data.[3] The choice of ω_c is supported by the fact that the characteristic phonon energy for this system is 13.4 meV, while the largest phonon energy does not exceed 30 meV. For the electron-phonon coupling constant, we use the phonon density of states (PDOS) calculated by Piekarz *et al.*,[19] opportunely scaled in order to obtain $\lambda_s = \lambda_d = 2.1$. It is worth noting that this is much larger than expected from *ab initio* calculations;[19] however, with these values, the effective electron-phonon coupling constant $\lambda_{s,eff}$, given by[14–16]

$$\lambda_{s,eff} = 2\int_0^{+\infty} d\omega \frac{N^N(\omega)}{N^N(0)} \int_0^{+\infty} d\Omega \frac{\alpha^2 F_s(\Omega)}{(\Omega-\omega)^2}, \qquad (7)$$

takes a value of $\lambda_{s,eff} = 3.6$, which can be positively compared with the enhancement factor for the electronic specific heat coefficient obtained in Ref. 20. We derive the remaining parameters by reanalyzing the normalized local spin susceptibility from the NMR experiment by Curro *et al.*,[3] as reported in Fig. 1; in particular, it is necessary to assume $\Gamma = 0.5$ meV to fit the shape of the curve,[13] while $\mu_d^* = 0.247$ fixes T_c to the value expected for a six-month-old sample (17.4 K). This corresponds to a value $\Gamma = 0.243$ meV for a fresh sample with $T_c = 18.5$ K. We note that, assuming d-wave symmetry for the gap function, the parameter μ_s^* does not enter into the two relevant Eliashberg equations. Therefore, although it is certainly larger than μ_d^*, it does not influence the solution. In the case of a pure s-wave gap, μ_d^* is not relevant and μ_s^* is fixed by the T_c of a fresh sample.

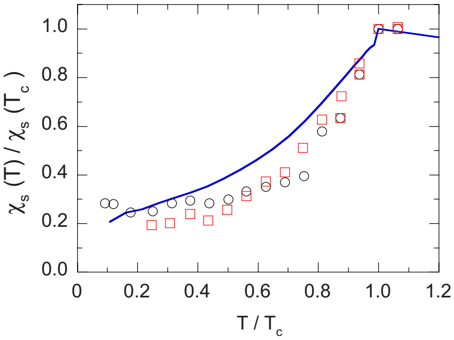

FIG. 1. (Color online) The normalized local spin susceptibility of PuCoGa_5 calculated from the real axis solution of the Eliashberg equations assuming a dirty d-wave gap function, $\Gamma = 0.5$ meV and $c = 0$ (solid line). The corresponding gap at $T = 0$ K is $\Delta = 3.41$ meV. The experimental values (symbols) are taken from Curro *et al.* (Ref. 3), and refer to a six-month-old sample.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Polycrystalline samples of $^{239}\text{PuCoGa}_5$ were synthesized by arc melting as described in Ref. 21. Electrical resistivity measurements were performed with a Quantum Design PPMS-9 platform, over the temperature range 1.8–300 K and in magnetic fields up to 9 T. The minimum temperature was limited by self-heating due to the α decay of ^{239}Pu. All measurements were performed on samples encapsulated to avoid radioactive contamination of the environment. Figure 2 shows the temperature dependence of the resistivity $\rho(T)$ measured for the same sample after different aging times. A significant decrease of the critical temperature T_c is ob-

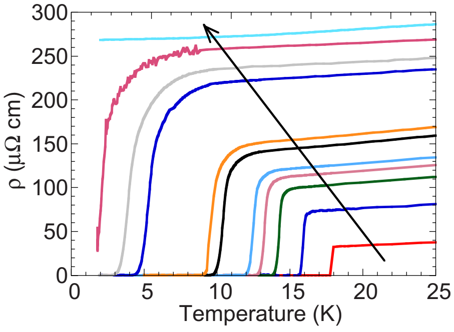

FIG. 2. (Color online) Temperature dependence of the electrical resistivity measured after different aging times, namely, 107, 408, 622, 736, 817, 1030, 1099, 1492, 1606, 1715, and 1815 days, in increasing order following the arrow.

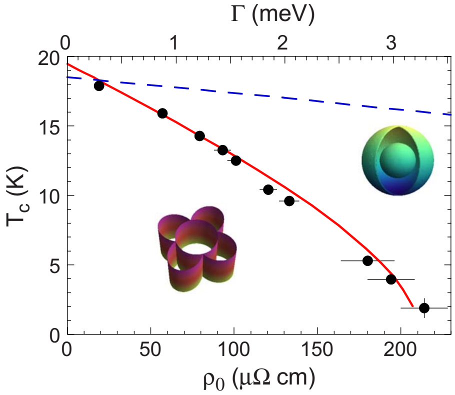

FIG. 3. (Color online) Critical temperature T_c of an aging polycrystalline ^{239}PuCoGa$_5$ sample as a function of the residual resistivity ρ_0. The corresponding values of the impurity scattering rate Γ are given in the upper horizontal scale. Solid and dashed lines correspond to calculations of T_c as a function of Γ, assuming d-wave and s-wave symmetries of the gap function, respectively.

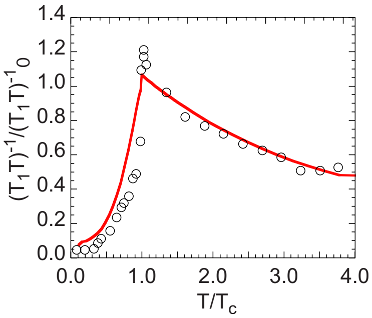

FIG. 4. (Color online) Normalized spin-lattice relaxation rate measured by Curro *et al.* (Ref. 3) in the normal and superconducting states of PuCoGa$_5$. The solid line has been calculated from the solutions of the Eliashberg equations used in this work.

served. After 1715 days, the prospective zero resistivity regime was below the minimum attainable temperature. No hints of superconductivity appear in the resistivity curve after 1815 days.

Figure 3 shows the variation of T_c during the aging as a function of the residual resistivity ρ_0. This latter quantity was obtained by a linear extrapolation to $T=0$ of the resistivity data just above T_c. It is directly related to the concentration of defects, and therefore, to the impurity scattering rate Γ. Indeed, ρ_0 is proportional to Γ/Ω_P^2; therefore, assuming that the plasma frequency Ω_P does not depend strongly on Γ, the ratio between ρ_0 and Γ is automatically fixed once the value of ρ_0 for the freshly prepared sample is known.

A marked decrease of T_c is observed for long aging times (corresponding to larger ρ_0 and larger Γ values). As displayed in Fig. 3, our calculations based on the solution of the Eliashberg equations show that the effect of self-irradiation damage on T_c is consistent with a d-wave superconductive regime with strong impurity scattering; in fact, a qualitatively different curve is expected for s-wave symmetry, as in this case, Γ does not enter directly in the Eliashberg equations, but only determines a broadening of the normal electron density of states.[22] In this sense, these measurements can be regarded as a test of the superconductive state, and confirm earlier indications given by NMR.[3]

Further evidence for nodal superconductivity was provided by measurements of the spin-lattice relaxation rate T_1^{-1} reported in Ref. 3. The temperature dependence of T_1^{-1} in the normal state of PuCoGa$_5$ was found to be qualitatively different than that observed in conventional BCS superconductors. This fact has been taken as evidence of a deviation from a Fermi-liquid-like normal state behavior just above T_c, and similarities with other non-Fermi-liquid materials, like the cuprates and the heavy-fermion CeCoIn$_5$ superconductor, have been put forward. In particular, the behavior of $T_1^{-1}T$ above T_c has been considered as an indication of spin-fluctuation mediated superconductivity.[3] To address this point, we calculated the T_1^{-1} temperature dependence in the framework of the model discussed here.[13] The results are compared against the data of Curro *et al.*[3] in Fig. 4. Although the agreement is not excellent, the observed behavior is certainly well reproduced. This indicates that it would be unwise to rest on the assumption that superconductivity in PuCoGa$_5$ is stabilized by magnetic fluctuations without searching for more stringent proofs. In this respect, it would be of paramount importance to determine the spectral function of magnetic fluctuations in PuCoGa$_5$. Inelastic neutron scattering measurements is the technique of choice, but, unfortunately, no large enough ^{242}PuCoGa$_5$ single crystals are yet available. Interesting results have been obtained for the antiferromagnetic, isostructural analog NpCoGa$_5$, where collective spin fluctuations emanating from the magnetic zone center (0 0 1/2) were observed to persist even in the paramagnetic phase.[4]

In order to obtain more detailed information on the nature of superconductivity in PuCoGa$_5$, we have extracted the values of the upper critical field B_{c2} from the $\rho(T,B)$ resistivity curves measured at different magnetic fields for an as-cast sample. The experimental values of B_{c2} are shown in Fig. 5 as a function of temperature, and compared with the results

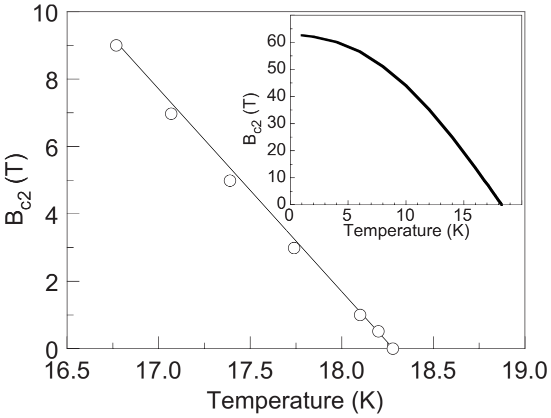

FIG. 5. The upper critical field B_{c2} measured as a function of temperature for a freshly prepared sample. The solid line represents the values calculated with the same parameters used to fit the local spin susceptibility and a Fermi velocity $v_F=0.861\times10^5$ m/s. The inset shows the $B_{c2}(T)$ curve calculated down to zero K.

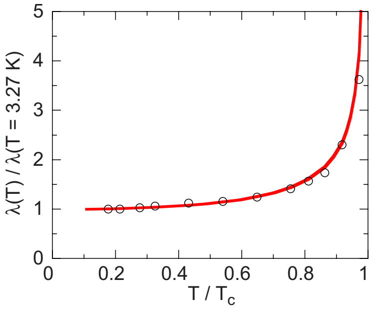

FIG. 6. (Color online) Calculated penetration depth compared against the experimental values of Morris *et al.* (Ref. 23).

of calculations carried out with the same values of the parameters given above and assuming a Fermi velocity $v_F = 0.861 \times 10^5$ m/s. While the experimental data points are limited for technical constraints to the region below 9 T, we have calculated the full B_{c2} vs T curve in the framework of the Eliashberg theory[14] (inset of Fig. 5), which extrapolates to a value of $B_{c2} \simeq 62.2$ T at $T=0$ K.

As shown in Fig. 6, we calculated the penetration depth $\lambda(T)$ and compared it with experimental data.[23] The agreement is as good as can be expected. From this calculation and from the low-temperature experimental value of λ, we get[10,24] a plasma energy $\Omega_p = 1.78$ eV. A hint about the nature of the superconductivity in $\mathrm{PuCoGa_5}$ is obtained by comparing this value of Ω_p with that resulting from a fit of the resistivity to the Boltzmann transport equation, following the procedure described in Ref. 25. Indeed, when the pairing is purely phonon mediated, the fit of $\rho(T)$ must contain the same electron-phonon-scattering matrix elements that appear in the Eliashberg solution of the superconducting state.[25] When this condition is imposed, and the transport electron-phonon coupling constant, λ_{tr}, is assumed to be equal to λ_s, a value of $\Omega_p = 2.69$ eV gives a good fit of the resistivity measured below 110 K for a freshly prepared sample (see Fig. 7). As $\rho / T \propto \lambda / \Omega_p^2$, to get $\Omega_p = 1.78$ eV from the resistivity fit, one should assume $\lambda_{tr} = 0.92$. This is quite a reasonable value, as $\lambda_s \geqslant \lambda_{tr}$,[26] and it shows that the transport properties of $\mathrm{PuCoGa_5}$ are compatible with the assumption of electron-phonon coupling. Attention should be paid to a possible anisotropic behavior of the penetration depth, as this quantity was measured on a single crystal, as opposed to the other experiments that made use of polycrystalline samples. This fact was not taken into account.

The inset of Fig. 7 shows that the normal state electrical resistivity near T_c can be reproduced in a satisfactory way by the general theory adopted in this paper in connection with a realistic PDOS. Previous electron-phonon coupling calculations[2] probably failed because a Debye PDOS approximation is not justified in this compound.[19]

Above 110 K, the calculated linear increase of the resistivity does not fit at all the measured curve, as it fails to reproduce the saturation observed at high temperature. This is a well known problem in A-15 and heavy-fermion superconductors.[27,28] The temperature dependence of the electrical resistivity of $\mathrm{PuCoGa_5}$ has been addressed by Bang *et al.*,[2] considering both spin fluctuations and phonons as mediating boson. For the phonon case, these authors show that the shunting model proposed by Calandra and Gunnarsson[29] is partially successful in reproducing the S-shaped behavior of the resistivity. Alternatively, the disagreement could be attributed to a failure of the one-band model used in the present calculation. As pointed out by Opahle and Oppeneer, a multiband approach may be necessary to describe the superconductivity in $\mathrm{PuCoGa_5}$, as a consequence of the bidimensionality of the Fermi sheets.[17] A second conduction band, as suggested for $\mathrm{MgB_2}$,[30] could resolve the discrepancy. Whatever the reason, we stress that the high-temperature behavior of the resistivity has no link with the physics underlying the superconducting phase.[2]

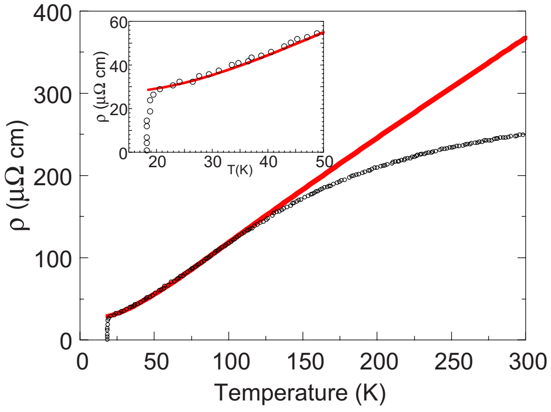

FIG. 7. (Color online) Electrical resistivity of the as-cast $^{239}\mathrm{PuCoGa_5}$ sample, measured as a function of temperature. The solid line is a fit to the Boltzmann transport equation in the normal state (Ref. 25). The electron-phonon-scattering matrix elements used for the fit are the same as those describing the superconducting state in the Eliashberg model. The inset is a close-up of the resistivity curve around T_c.

IV. CONCLUSIONS

We have experimentally and theoretically investigated the role of self-induced defects and disorder in modifying the superconductive properties of $\mathrm{PuCoGa_5}$. Our experimental results are consistent with a dirty *d*-wave model for superconductivity with strong impurity scattering. We show that results of key experiments probing superconductive parameters (critical temperature, upper critical field, penetration depth) on this compound can be well reproduced by assuming a phononic mechanism for superconductivity in the framework of the Eliashberg theory, which also accounts for reasonable values of $\lambda_{s,eff}$ (as inferred from specific heat) and Ω_p (deduced from the electrical resistivity). Although the analysis we have discussed in this paper cannot be considered a proof that phonons act as electron pairing mediators in $\mathrm{PuCoGa_5}$, it shows at least that sound evidence for the occurrence of magnetic pairing in this compound has not yet been provided. More selective experiments are required to clarify the role of magnetic fluctuations in $\mathrm{PuCoGa_5}$.

ACKNOWLEDGMENTS

The high-purity plutonium metal required for the fabrication of the compounds was made available through a loan agreement between Lawrence Livermore National Laboratory and ITU, in the frame of a collaboration involving LLNL, Los Alamos National Laboratory, and the U. S. Department of Energy.

---

*Present address: Belgian Nuclear Research Center, Boeratang 200, 2400 Mol, Belgium.

[1] J. L. Sarrao, L. A. Morales, J. D. Thompson, B. L. Scott, G. R. Stewart, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, and G. H. Lander, Nature (London) **420**, 297 (2002).

[2] Y. Bang, A. V. Balatsky, F. Wastin, and J. D. Thompson, Phys. Rev. B **70**, 104512 (2004).

[3] N. J. Curro, T. Caldwell, E. D. Bauer, L. A. Morales, M. J. Graf, Y. Bang, A. V. Balatsky, J. D. Thompson, and J. L. Sarrao, Nature (London) **434**, 622 (2005).

[4] N. Magnani, A. Hiess, R. Caciuffo, E. Colineau, F. Wastin, J. Rebizant, and G. H. Lander, Phys. Rev. B **76**, 100404(R) (2007).

[5] G. Ghigo, G. A. Ummarino, R. Gerbaldo, L. Gozzelino, F. Laviano, and E. Mezzetti, Phys. Rev. B **74**, 184518 (2006).

[6] E. M. Jackson, B. D. Weaver, G. P. Summers, P. Shapiro, and E. A. Burke, Phys. Rev. Lett. **74**, 3033 (1995).

[7] J. Giapintzakis, D. M. Ginsberg, M. A. Kirk, and S. Ockers, Phys. Rev. B **50**, 15967 (1994).

[8] F. Jutier, J.-C. Griveau, C. J. van der Beek, E. Colineau, F. Wastin, J. Rebizant, P. Boulet, T. Wiss, H. Thiele, and E. Simoni, Europhys. Lett. **78**, 57008 (2007).

[9] G. M. Eliashberg, Sov. Phys. JETP **3**, 696 (1963).

[10] J. P. Carbotte, Rev. Mod. Phys. **62**, 1028 (1990).

[11] C. T. Rieck, D. Fay, and L. Tewordt, Phys. Rev. B **41**, 7289 (1990).

[12] G. A. Ummarino, D. Daghero, and R. S. Gonnelli, Physica C **377**, 292 (2002).

[13] J. P. Carbotte and C. Jiang, Phys. Rev. B **49**, 6126 (1994).

[14] B. Mitrovich and J. P. Carbotte, Can. J. Phys. **61**, 872 (1983).

[15] B. Mitrovich and J. P. Carbotte, Can. J. Phys. **61**, 784 (1983).

[16] B. Mitrovich and J. P. Carbotte, Can. J. Phys. **61**, 758 (1983).

[17] I. Opahle and P. M. Oppeneer, Phys. Rev. Lett. **90**, 157001 (2003).

[18] K. A. Musaelian, J. Betouras, A. V. Chubukov, and R. Joynt, Phys. Rev. B **53**, 3598 (1996).

[19] P. Piekarz, K. Parlinski, P. T. Jochym, A. M. Oleś, J. P. Sanchez, and J. Rebizant, Phys. Rev. B **72**, 014521 (2005).

[20] T. Maehira, T. Hotta, K. Ueda, and A. Hasegawa, Phys. Rev. Lett. **90**, 207007 (2003).

[21] P. Boulet, E. Colineau, F. Wastin, J. Rebizant, P. Javorský, G. H. Lander, and J. D. Thompson, Phys. Rev. B **72**, 104508 (2005).

[22] C. M. Soukoulis and D. A. Papaconstantopoulos, Phys. Rev. B **26**, 3673 (1982).

[23] G. D. Morris, R. H. Heffner, E. D. Bauer, L. A. Morales, J. L. Sarrao, M. J. Fluss, D. E. MacLaughlin, L. Shu, and J. E. Anderson, Physica B **374-375**, 180 (2006).

[24] A. A. Golubov, A. Brinkman, O. V. Dolgov, J. Kortus, and O. Jepsen, Phys. Rev. B **66**, 054524 (2002).

[25] P. B. Allen, Phys. Rev. B **17**, 3725 (1978).

[26] J. J. Joyce, J. M. Wills, T. Durakiewicz, M. T. Butterfield, E. Guziewicz, J. L. Sarrao, L. A. Morales, A. J. Arko, and O. Eriksson, Phys. Rev. Lett. **91**, 176401 (2003).

[27] Z. Fisk and G. W. Webb, Phys. Rev. Lett. **36**, 1084 (1976).

[28] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, Phys. Rev. Lett. **52**, 679 (1984).

[29] M. Calandra and O. Gunnarsson, Phys. Rev. B **66**, 205105 (2002).

[30] I. I. Mazin, O. K. Andersen, O. Jepsen, O. V. Dolgov, J. Kortus, A. A. Golubov, A. B. Kuzmenko, and D. van der Marel, Phys. Rev. Lett. **89**, 107002 (2002).