Magnetic field dependence of the precursor diamagnetism in La superconductors with magnetic Pr impurities

F Soto, C Carballeira, J M Doval, J Mosqueira, M V Ramallo, A Ramos-Álvarez, D Sóñora, J C Verde and F Vidal

LBTS, Departamento de Física da Materia Condensada, Universidade de Santiago de Compostela, ES-15782 Santiago de Compostela, Spain

E-mail: j.mosqueira@usc.es

Received 5 December 2014, revised 19 March 2015
Accepted for publication 30 March 2015
Published 7 May 2015

Abstract
The interplay between fluctuating Cooper pairs and magnetic impurities in conventional BCS low-$T_c$ superconductors has been studied through measurements of the magnetic field dependence of the fluctuation diamagnetism (FD) above $T_c$ in lanthanum with praseodymium impurities. These measurements provide a crucial confirmation of our previous observation (F Soto et al 2006 Europhys. Lett. 73 587) that in the dilute impurity regime the FD increases almost linearly with the concentration of magnetic impurities. This striking effect is attributed to a variation due to the presence of the fluctuating Cooper pairs of the coupling between magnetic impurities. To describe these results at a phenomenological level, we propose a Gaussian Ginzburg–Landau model for the FD which includes an indirect contribution proportional to both the concentration of impurities and the density of the Cooper pairs. Our approach is able to explain simultaneously the FD increase due to magnetic impurities and its decrease with the application of large magnetic fields.

Keywords: superconductivity, magnetic properties, fluctuations

(Some figures may appear in colour only in the online journal)

1. Introduction

The interplay between magnetism and superconductivity is still present an open and interesting subject of strongly correlated electron systems [1]. This topic was broached by Matthias et al [2, 3] more than 50 years ago when they studied the decrease of the superconducting transition temperature ($T_c$) of lanthanum due to the introduction of magnetic rare earth impurities, an effect later explained in terms of pair breaking by Abrikosov and Gor’kov [4]. In spite of the interest in this topic, to our knowledge only a few works have addressed the interplay between magnetic impurities and the Cooper pairs created in the normal state by thermal agitation (the so-called superconducting fluctuations [5, 6]), most of them dealing with the fluctuation-induced electrical conductivity (or paraconductivity), $\Delta \sigma$ [7–9].

As suggested early on, on theoretical grounds, by Schmidt [10], magnetic impurities may enhance $\Delta \sigma$ through a change in the relaxation time of fluctuating Cooper pairs. Therefore, it may be expected that a static observable like the fluctuation magnetic susceptibility $\Delta \chi$ will be unaffected by magnetic impurities, apart from the effects associated with possible changes in the superconducting parameters. (For a recent theoretical work on this issue see, e.g., [11].) This is in fact the case with high-$T_c$ cuprates: recent measurements [12] have shown that the fluctuation diamagnetism (FD) of optimally doped YBa$_2$Cu$_3$O$_{6.5}$ is not appreciably affected by the presence of magnetic impurities (either in the CuO$_2$ planes or intercalated between them). In striking contrast, the measurements in lanthanum with diluted magnetic (Pr) impurities presented in [13] have shown an important enhancement of FD, that is observed to be considerably larger than the theoretical results for three-dimensional isotropic superconductors [5, 6, 14–19]. The enhancement was found to be proportional to the concentration of impurities, being as large as a factor of 5 for a Pr concentration of 2 at.%. This effect was attributed to...
Table 1. Summary of the superconducting parameters of the samples studied. The $T_c$ and $\Delta T_c$ values were obtained from the temperature dependence of the field-cooled magnetic susceptibility measured with $\mu_0 H = 0.5$ mT. $H_{c2}(0)$ and $\kappa$ were estimated from the reversible mixed-state magnetization (obtained as the average of the field-up and field-down measurements). The coherence length amplitudes were obtained as $\xi(0) = (\phi_0/2\mu_0 H_{c2}(0))^2$. The mean free paths were estimated from the resistivity just above $T_c$ by using a Drude model. For details see [21].

| Sample | $T_c$ | $\Delta T_c$ | $\mu_0 H_{c2}(0)$ | $\xi(0)$ | $\kappa(T_c)$ | $\ell$ |
|--------|-------|--------------|-------------------|-----------|---------------|-------|
| Pr at.% | (K)   | (K)          | (T)               | (nm)      |               | (nm)  |
| 0      | 5.85  | 0.16         | 0.8               | 20        | 4.4           | 26.5  |
| 0.5    | 5.69  | 0.12         | 0.9               | 19        | 5.6           | 15.0  |
| 1      | 5.51  | 0.25         | 0.9               | 18        | 6.0           | 11.0  |
| 2      | 5.40  | 0.18         | 1.0               | 18        | 6.4           | 7.5   |

a change in the coupling between magnetic ions (mediated by conduction electrons) due to the presence of the fluctuating Cooper pairs [13]. Nevertheless, those results were also affected by the experimental uncertainties associated with the strong temperature dependence near $T_c$ (Curie-like) of the normal state background, and thus further experimental studies of these striking results are highly desirable.

Here we present measurements of the magnetic-field dependence of $\Delta \chi$ just above $T_c$ in La and La–Pr alloys. The fields used span from $5 \times 10^{-3}$ T to 3 T, the latter value being three times larger than the upper critical field of the studied samples, where fluctuation effects are expected to be negligible [6, 20]. The interest in these new measurements is twofold: on the one hand, the smooth $H$-dependence of $\chi$ in the normal state will allow a reliable determination of $\Delta \chi$ and verification of the enhancement with the concentration of impurities found in [13]. On the other hand, these new data will make it possible to study, for the first time in superconductors with magnetic impurities, the finite-field (or Prange) regime, where fluctuation effects are expected to be strongly reduced with respect to the zero-field limit [6, 20].

2. Experimental details and results

The samples used in this work (pure La and La–Pr alloys) are commercial (Alfa–Aesar and Goodfellow, respectively; 99.9% purity). They were used in the previous experiments of [13], and a thorough characterization may be found in [21]. The resulting superconducting parameters are summarized in table 1. The $T_c$ values and the transition widths, $\Delta T_c$, were estimated from the temperature dependence of the low-field magnetic susceptibility. In the case of pure La, the transition temperature is between those of pure $\alpha$-La ($\sim 5.0$ K) and $\beta$-La ($\sim 6.0$ K) [22–28], but no traces of diamagnetic steps were observed near the latter temperatures. This is consistent with the mixing of both crystallographic phases at lengths of the order of or smaller than the superconducting coherence length amplitude $\xi(0)$ ($\sim 20$ nm; see table 1). The $\Delta T_c$ values are about 3% of the corresponding $T_c$ values, which will allow us to analyze fluctuation effects above $T_c$ down to reduced temperatures $\varepsilon \equiv \ln(T/T_c) \sim 0.03$. In the presence of a magnetic field, the $T_c(H)$ shift to lower temperatures further increases the accessible temperature range. The Ginzbarg–Landau (GL) parameter at $T_c$, $\kappa(T_c)$, and the upper critical field (linearly extrapolated to $T = 0$ K), $H_{c2}(0)$, were obtained from magnetization measurements in the mixed state. In view of the $\kappa(T_c)$ values, even pure La is a type-II superconductor, in agreement with earlier results of Pan and coworkers [28]. We are not aware of previous $H_{c2}$ measurements in La–Pr alloys, but the results found in pure La are consistent with those in the literature. For instance, in [23, 25, 26, 28] a thermodynamic critical magnetic field $\mu_0 H_{c2}(0) \sim 80–84$ mT is found for $\alpha$-La and 110-160 mT for $\beta$-La. By using the relation $\mu_0 H_{c2}(0) = \mu_0 H_{c2}(0)/\sqrt{2} \kappa$ and the data in table 1, a result of $\mu_0 H_{c2}(0) \approx 95$ mT is obtained, well within these last values. Finally, electron mean free paths at low temperatures (estimated from the residual resistivities) are of the order of or smaller than the corresponding $\xi(0)$, so the samples may be considered close to the dirty limit1. This excludes the presence of non-local effects on FD and therefore allows an easier comparison with the GL predictions.

The magnetization measurements were performed with a commercial SQUID magnetometer (Quantum Design). To use all the available volume in the sample space, the samples were cut as cylinders 6 mm in height and 6.5 mm in diameter. In figure 1 we present the magnetic susceptibility of all the studied samples as a function of the magnetic field at a selected reduced temperature, $\varepsilon \equiv \ln(T/T_c) = 0.06$. Even La with 0% Pr presents paramagnetic behavior, probably due to the presence of a small amount ($\leq 0.1\%$) of magnetic rare-earth impurities. The data in figure 1 are already corrected for a small upturn ($\leq 1\%$ of the normal state contribution) appearing typically below 0.15 T (see figure 2(a)). This effect is of unknown origin2, but it is unrelated to superconductivity because it is present in all isotherms up to well above $T_c$ ($\varepsilon = 0.5$), where superconducting fluctuations are expected to be negligible [29]. Therefore, we took advantage of the temperature independence and corrected the isotherms in the fluctuation region near $T_c$ by subtracting the anomaly observed at $\varepsilon = 0.5$. An example of such a correction is shown in figure 2. In any case this low-field anomaly is of no consequence in our analysis because it occurs strictly in the high-$H$ region.

The fluctuation-induced magnetic susceptibility $\Delta \chi$ may be obtained from the data in figure 1 by subtraction of the (field-dependent) normal-state contribution. This was estimated for each sample by fitting a quadratic polynomial in the interval $\sim (0.6–2) H_{c2}(0)$. The resultant background contributions are represented as solid lines in figure 1. The fitting function was chosen because it agrees with the data with good accuracy (the maximum deviation in the fitting region is

1 In the case of nominally pure La, this is consistent with the presence in the sample of a small amount of rare-earth impurities.

2 It cannot be attributed to the paramagnetic contribution of the magnetic impurities because it should be $H$-independent when $H \rightarrow 0$. We also discarded the possibility of it being an artifact associated a possible remnant magnetic field in the superconducting coil after being set in persistent mode.
0.5%) and extrapolates smoothly to the lowest fields. Note that to get better precision in determining the background contribution in the low-field region, we extended the lower bound of the fitting region down to 0.6 $H_c^2(0)$, neglecting the small fluctuation effects that may be present up to $\sim H(0)$ [20].

Fluctuation effects may already be appreciated in figure 1 as a $\chi(H)$ reduction with respect to the background contribution for fields below $\sim 0.5 H_c^2(0)$. The amplitude of this effect is roughly proportional to the Pr concentration, as shown in figure 3. As already commented in the introduction, this striking effect was already observed in measurements of the FD against temperature in the low-field limit [13]. The present measurements confirm those experimental findings and will make it possible to study the $\Delta \chi$ behavior in the presence of large reduced magnetic fields (in the so-called Prange fluctuation regime).

3. Data analysis

The $\Delta \chi$ data will be analyzed in terms of a GL approach with Gaussian fluctuations of the superconducting order parameter (GGL approach) [5, 6]. The direct contribution to $\Delta \chi$ (due to the Cooper pairs created by thermal fluctuations above $T_c$) was calculated in [19] (see also [18, 30]) by using a
continuous Landau-level approximation (expected to be useful for reduced fields up to $h \approx 0.3$) [19]. This approach includes a total-energy cutoff to take into account the existence of a limit (of the order of the actual $T = 0$ $K$ coherence length) to the shrinkage of the superconducting wavefunction at high reduced magnetic fields or temperatures. The resultant expression is

$$
\Delta\chi^{\text{GGL}} = -\frac{2\mu_0 k_B T_F^{(0)}}{\phi_0^2 h} \int_{0}^{\pi} dq \left[ \frac{c - \epsilon}{2h} \right]
$$

$$
- \left( \frac{c + q^2}{2h} \right)^{\nu} \left[ \frac{c + h + q^2}{2h} \right] + \ln \Gamma \left( \frac{c + h + q^2}{2h} \right)
$$

$$
+ \left( \frac{\epsilon + q^2}{2h} \right)^{\nu} \left[ \frac{\epsilon + h + q^2}{2h} \right] - \ln \Gamma \left( \frac{\epsilon + h + q^2}{2h} \right)
$$

$$
\Delta\chi^{\text{GGL}} = - \frac{\mu_0 k_B T_F^{(0)}}{3\phi_0^2 T_F^{(0)}} \left( \frac{\text{atan} \left( \frac{c - \epsilon}{\sqrt{\epsilon}} \right)}{\sqrt{\epsilon}} - \frac{\text{atan} \left( \frac{c - \epsilon}{\sqrt{\epsilon}} \right)}{\sqrt{\epsilon}} \right)
$$

where $\Gamma$ and $\psi$ are, respectively, the gamma and digamma functions, $k_B$ is the Boltzmann constant, $\phi_0$ the flux quantum, and $c \approx 0.55$ is the cutoff constant [29]. This expression includes as a particular case the low-field (or Schmidt regime ($h \ll \epsilon$), in which $\Delta\chi$ is field-independent: by imposing $h \ll \epsilon$ in equation (1) we obtain

$$
\Delta\chi^{\text{GGL}} = -\frac{\mu_0 k_B T_F^{(0)}}{3\phi_0^2 T_F^{(0)}} \left( \frac{\text{atan} \left( \frac{c - \epsilon}{\sqrt{\epsilon}} \right)}{\sqrt{\epsilon}} - \frac{\text{atan} \left( \frac{c - \epsilon}{\sqrt{\epsilon}} \right)}{\sqrt{\epsilon}} \right)
$$

which in absence of cutoff ($c \to \infty$) leads to the classical Schmidt result $\Delta\chi = -\mu_0 k_B T_F^{(0)}/6\phi_0^2 \sqrt{\epsilon}$ [14]. Equations (1) and (2) predict the vanishing of $\Delta\chi$ at $\epsilon = c$, the reduced temperature at which the GL coherence length $\xi(\epsilon)$ becomes comparable to $\xi_{\text{GGL}}$ [29].

The $h$-dependence of $\Delta\chi$ for all the studied Pr concentrations is shown in figure 4. To compare the results obtained in the different samples, taking into consideration equation (1) these data are normalized by $\xi(0)/T$. As expected [18, 20], the experimental $\Delta\chi$ for pure La is in good agreement with equation (1). However, the $\Delta\chi$ amplitude increases with the Pr content (almost linearly, as shown in figure 3). Moreover, on increasing the concentration of impurities the $h$-dependence becomes less pronounced. This experimental evidence suggests that the magnetic impurities enhance some contribution in addition to $\Delta\chi^{\text{GGL}}$ having a smoother $h$-dependence. As first suggested in [13], a natural candidate for the origin of such a contribution is the variation of the coupling between magnetic (Pr) impurities due to the condensation of Cooper pairs. The argument is as follows: in alloys with diluted magnetic impurities, the main vehicle for the interactions between these impurities is the electronic sea. A small variation in the density of normal electrons is expected to linearly vary the coupling strength between these impurities (e.g., through the variation of the effective Fermi vector, $k_F$, and the self-energy, $\Sigma$, of superconducting fluctuations) also leads to contributions to $\Delta\chi$ proportional to $n_S$. For that, we apply to our $h \neq 0$ case the same procedure as used in [29] for $h = 0$ and replace the $h = 0$ fluctuation spectrum $\epsilon + \xi^2(0)k^2$ with the $h > 0$ one, $\epsilon + (2\eta + 1)h + \xi^2(0)k^2$. Here $k$ is the fluctuation wave vector, $k_F$ is its component perpendicular to the applied magnetic field, and $n = 0, 1, \ldots$ is the Landau-level index.
The GGL fluctuation-averaged superfluid density is then
\[
n_S = \left\langle |\Psi|^2 \right\rangle \propto \sum_{k,n} \frac{hT}{\varepsilon + (2n + 1)h + \xi^2(0)k^2} \tag{4}
\]
where \( \left\langle |\Psi|^2 \right\rangle \) indicates the statistical and spatial average of the squared modulus of the GL wavefunction. Note the appearance in the \( \sum_{k,n} \) summation of the \( hT \) prefactor, which is due to the Boltzmann statistical weight and to the degeneration of each Landau level. The summation of equation (4) then becomes possible using the same continuous Landau-level approach and total-energy cutoff procedure as used in [19] to obtain equation (1). The result is then (employing the same arbitrary dimensionless units as in [29])
\[
n_S = \frac{\mu_0 e^2 k_B T_e(0)}{2h^2} \int_0^{\phi_{\pi\pi}} dq \left[ \psi\left(\frac{\varepsilon + h + q^2}{2h}\right) - \psi\left(\frac{\varepsilon + h + q^2}{2h}\right) \right] \tag{5}
\]
The solid lines in figure 4 are the best fit of
\[
\Delta \chi^{GGL}(\varepsilon, h) + A \times n_S(\varepsilon, h) \tag{6}
\]
to the \( \Delta \chi(h) \) data for \( \varepsilon = 0.06 \). The fitting region extends up to \( h = 0.3 \), where the aforementioned approaches are expected to be applicable. Given that the data in this figure are already normalized by \( \xi(0)T \), the only free parameter is \( A \). The agreement is excellent, in some cases even above \( h = 0.3 \). The resultant \( A \) value (−0.5) is reasonably close to that obtained in [13] from low-field \( \Delta \chi \) measurements against the temperature (\( A \approx -0.7 \)), taking into account the important uncertainties associated with the background subtraction in this last case (mainly affecting the \( \Delta \chi \) amplitude). The data in the region \( h > 0.3 \) can be fitted to the empirical formula
\[
-\Delta \chi/\xi(0)T = (0.25 + 0.6x)h^{-2},
\]
indicating then that the extra \( \Delta \chi \) contribution due to Pr ions maintains its proportionality with \( x \) also for \( h \lesssim 0.3 \).

It is worth noting that Legvold et al [35] have shown that the \( T_e \) depression with the Pr concentration in La–Pr (which is consistent with the Abrikosov–Gor’kov theory; see figure 5(a)) is close to that of non-magnetic La–Y and La–Lu alloys. This led them to suggest that Pr in the La–Pr alloy could be in a singlet state and that there is little evidence for Pr–Pr interactions in these materials. In relation to this, in a recent paper Kogan and Prozorov [36] calculated that if the upper critical field increases with the concentration of impurities the system may not be in the purely magnetic scattering regime, and non-magnetic scattering should also be taken into account. However, our observed \( H_{c2}(0) \) variation with the Pr concentration is quite similar to the experimental uncertainty. For this reason, in our simplified model we have ignored a possible contribution coming from non-magnetic scattering. Also, the linear increase in magnetic susceptibility in the normal state with the Pr concentration (see figure 5(b)) clearly indicates that Pr does introduce some moderate additional magnetic moment into the alloy. Our results thus currently indicate that even these relatively weak magnetic moments (even if they perhaps do not dominate the \( T_e(x) \) shift) may profoundly affect the diamagnetic contribution coming from superconducting fluctuations above \( T_e \).

The present results contrast with the behavior observed in high-\( T_e \) cuprates, where magnetic impurities (within the CuO2 layers or intercalated between them) lead to not appreciable effects in the fluctuation-induced magnetic susceptibility once the change in the \( T_e \) value is taken into account. This suggests that in these materials the pairs created above \( T_e \) by thermal fluctuations lead to a negligible effect on the interaction between magnetic impurities.

4. Conclusions

We have presented detailed measurements of the diamagnetism induced by superconducting fluctuations in a BCS superconductor (La) under the simultaneous presence of magnetic impurities (Pr) and external magnetic fields. It was found that magnetic fields approaching the upper critical field at \( T \rightarrow 0 \) K are very effective in reducing the fluctuation effects. However, counterintuitively at first, the magnetic impurities lead to an important enhancement of the amplitude of the fluctuation magnetic susceptibility. This enhancement is roughly proportional to the concentration of magnetic impurities and is as large as one order of magnitude for concentrations of only 2 at. % of Pr.

The experimental data are interpreted in terms of a change of the coupling between magnetic impurities (mediated by conduction electrons), induced by the presence of

\[3\] See [21], where the \( H_{c2}(0) \) values were obtained from measurements of the reversible magnetization in the mixed state. Due to the highly irreversible nature of the latter in La–Pr alloys, \( H_{c2}(0) \) was obtained as the average of the field-up and field-down contributions. The uncertainty associated with this procedure is comparable with the seeming variation of \( H_{c2}(0) \) with \( x \).
fluctuating Cooper pairs. In accordance with this, to analyze the experimental data we proposed a Gaussian Ginzburg–Landau model for $\Delta \chi$ which includes an indirect contribution proportional to the concentration of impurities, $x$, and to the density of the Cooper pairs, $n_S$. This approach includes a total-energy cutoff to account for the short-wavelength modes excited in high reduced magnetic fields and is expected to be applicable up to $\sim 0.3 H_0(0)$. The agreement with the experimental data is excellent in a wide magnetic field interval and, for all the concentrations of impurities studied, in agreement with previous findings in the low-field limit [13]. It would be interesting to further investigate whether fully microscopic approaches may account for the amplitude of the impurity-induced enhancement of the FD.

Acknowledgments

This work was supported by the Spanish MICINN (Grant No. FIS2010–19807) and by the Xunta de Galicia (Grant No. GPC2014/038). A R-A acknowledges support through an FPI grant (no. BES-2011-046820).

References

[1] See, e.g. Scalapino D J 2012 Rev. Mod. Phys. 84 1383
[2] Matthias B T, Suhl H and Corenzwit E 1958 Phys. Rev. Lett. 1 92
[3] Hein R A, Falge R L Jr., Matthias B T and Corenzwit C 1969 Phys. Rev. Lett. 2 500
[4] Abrikosov A A and Gor’kov L P 1961 Sov. Phys. JETP 12 1243
[5] See, e.g. Tinkham M 1996 Introduction to superconductivity (New York: McGraw-Hill) ch 8
[6] Skocpol W J and Tinkham M 1975 Rep. Prog. Phys. 38 1049
[7] Vidal F et al 1988 Physica C 156 165
[8] Lindqvist P, Nordström A and Rapp O 1990 Phys. Rev. Lett. 64 2941
[9] Spahn E and Keck K 1990 Physica B 165-166 1357
[10] Schmidt H 1968 Phys. Lett. 27A 658
[11] Borycki D 2014 Eur. Phys. J. B 87 118
[12] Soto F et al 2013 Supercond. Sci. Technol. 26 045007
[13] Soto F, Cabo L, Mosquera J, Ramallo M V, Veira J A and Vidal F 2006 Europhys. Lett. 73 587
[14] Schmid A 1968 Phys. Rev. 180 527
[15] Gollub J P, Beasley M R, Newbower R S and Tinkham M 1969 Phys. Rev. Lett. 22 1288
[16] Gollub J P, Beasley M R and Tinkham M 1970 Phys. Rev. Lett. 25 1646
[17] Gollub J P, Beasley M R, Callarotti R and Tinkham M 1973 Phys. Rev. B 7 3039
[18] Mosquera J, Carballeira C and Vidal F 2001 Phys. Rev. Lett. 87 144508
[19] Carballeira C, Mosquera J, Ramallo M V, Veira J A and Vidal F 2001 J. Phys.: Condens. Matter 13 9271
[20] Soto F et al 2004 Phys. Rev. B 70 060501
[21] Soto F, Mosquera J, Ramallo M V and Vidal F 2006 Physica B 378-380 409
[22] Leslie J D et al 1964 Phys. Rev. 134 A309
[23] Anderson G S, Legvold S and Spedding F H 1958 Phys. Rev. 109 243
[24] Berman A, Zemansky M W and Boorse H A 1958 Phys. Rev. 109 70
[25] Finnemore D K, Johnson D L, Ostenson J E, Spedding F H and Beaudry B J 1965 Phys. Rev. 137 A550
[26] Johnson D L and Finnemore D K 1967 Phys. Rev. 158 376
[27] Legvold S, Burgardt P, Beaudry B J and Gschneidner K A Jr. 1977 Phys. Rev. B 16 2479
[28] Pan P H et al 1980 Phys. Rev. B 21 2809
[29] Vidal F et al 2002 Europhys. Lett. 59 754
[30] Mosquera J et al 2003 J. Phys.: Condens. Matter 15 3283
[31] Anderson P W and Suhl H 1959 Phys. Rev. 116 898
[32] Jensen J and Hedegård P 2004 J. Magn. Magn. Mater. 272-276 E177
[33] Nøgaard K et al 2000 Phys. Rev. Lett. 84 4982
[34] Bergeret F S, Volkov A F and Efetov K B 2004 Europhys. Lett. 66 111
[35] Legvold S, Green R W, Beaudry B J and Ostenson J E 1976 Solid State Commun. 18 725
[36] Kogan V G and Prozorov R 2013 Phys Rev B 88 024503