Doping-dependent reduction of the Cu nuclear magnetic resonance intensity in the electron-doped superconductor $Pr_{2-x}Ce_xCuO_4$

G. V. M. Williams[1] and J. Haase[2]
[1]*The MacDiarmid Institute, Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand*
[2]*Faculty of Physics and Earth Science, Universität Leipzig, Linnéstrasse 5, D-04103 Leipzig, Germany*
(Received 31 January 2007; published 21 May 2007)

^{63}Cu nuclear magnetic resonance (NMR) measurements on the electron-doped high-temperature superconducting cuprates $Pr_{2-x}Ce_xCuO_4$ reveal a large temperature-dependent reduction in the Cu NMR intensity for $x \leqslant 0.125$ and below room temperature. Our results show that the previous report of a reduction in the ^{63}Cu NMR intensity in $Sr_{0.9}La_{0.1}CuO_2$ with 0.1 doped electrons per Cu is not specific to this superconductor. Rather, the doping-dependent reduction appears to be intrinsic to the electron-doped superconductors. Our results provide further evidence that there is a symmetry in the electron-doped and hole-doped superconducting phase diagrams where a significant temperature-dependent reduction of the Cu NMR intensity occurs for less than ~0.13 doped holes or doped electrons per Cu.

DOI: 10.1103/PhysRevB.75.172506 PACS number(s): 74.72.−h, 74.25.Ha, 74.25.Nf

Understanding the high-temperature superconducting cuprates (HTSCs) has been complicated by a reduction or wipeout of the Cu NMR intensity that has been reported from studies on some of the hole-doped high-temperature superconducting cuprates (HDHTSCs). Specifically, a large decrease in the Cu NMR intensity occurs in the $La_{2-x}Sr_xCuO_4$ and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ families of HDHTSCs that is large when the number of doped holes per copper is less than ~0.13.[1–4] A complete temperature-dependent wipeout of the Cu NMR intensity is observed for certain values of x and y in $La_{2-x-y}(Nd,Eu)_ySr_xCuO_4$ (Refs. 1 and 5–8), and a static charge-ordered state has been reported in $La_{1.875}Ba_{0.125}CuO_4$ that leads to a complete suppression of the superconducting state.[1,7,9]

The appearance of a reduction or wipeout of the Cu NMR intensity in some of the HDHTSCs has been attributed to phenomena that include charge-stripe ordering[10] or a slowing down of the spin dynamics.[5] It may arise from a temperature-dependent slowing down of the dynamic inhomogeneities that have been reported in low-energy inelastic neutron-scattering measurements.[11–14] These dynamic inhomogeneities have been interpreted in terms of dynamic phase separation into hole-rich and hole-poor regions.[15–17]

The effect of a slowing down of the dynamic inhomogeneities on the spin dynamics can be illustrated with a simple model where a Lorentzian spectral density of spin fluctuations is assumed. In this case, the spin-lattice relaxation rate $1/T_1$ can be written as $1/T_1 = \gamma^2 h_0^2 \tau_c/(1+\omega_L^2\tau_c^2)$, where h_0 is the magnitude of the fluctuating local field at the nucleus, $\hbar\omega_L$ is the energy of the nuclear Zeeman splitting, and τ_c is the characteristic spin-fluctuation time. A slowing down of the fast electronic spin fluctuations can occur via a temperature-dependent increase in τ_c that causes $1/T_1$ to increase and $1/T_1$ will maximize when $\tau_c = 1/\omega_L$. In the case of the Cu nuclei, T_1 can become too short for the NMR spectra to be observed, resulting in a loss of the Cu NMR signal. The Cu NMR signal can be partially recovered at low temperatures where $1/\tau_c$ is much less than ω_L, which has been experimentally observed in some HDHTSCs.[1,6,9] A slowing down will also lead to a peak in the La $1/T_1$ in $La_{2-x-y}(Nd,Eu)_ySr_xCuO_4$, which has also been reported.[2,5,8]

We have recently shown that a reduction of the Cu NMR intensity also occurs in the $Sr_{0.9}La_{0.1}CuO_2$ electron-doped HTSC (EDHTSC) but not the $Pr_{1.85}Ce_{0.15}CuO_4$ EDHTSC.[18] These superconductors represent the two classes of EDHTSCs. However, it is not known if the appearance of a Cu NMR intensity reduction is somehow intrinsic only to the $Sr_{0.9}La_{0.1}CuO_2$ EDHTSC because it is not possible to make good quality samples with La concentrations different from 0.1. For this reason, we have performed a study of the Cu NMR intensity in $Pr_{2-x}Ce_xCuO_4$ extending from $x=0.10$ to $x=0.20$ and report our results in this Brief Report. We show that there is a reduction in the Cu NMR intensity only for $x \leqslant 0.125$.

The synthesis of $Pr_{2-x}Ce_xCuO_4$ is reported elsewhere.[19] T_c was measured using a superconducting quantum interference device magnetometer and applied magnetic fields of 2 mT. The T_c values were 19, 21, 23, and 17 K for $x=0.10$, 0.125, 0.15, and 0.20, respectively. These values are similar to those obtained by Brinkmann *et al.*[20] Some of the samples were also c axis aligned in an epoxy resin in a magnetic field of 0.8 T, as described previously.[19]

Cu NMR measurements were made in an applied magnetic field of 9.2 T using a Hahn echo sequence, $\tau_{\pi/2}-\tau-\tau_\pi-\tau$, where the pulses $\tau_{\pi/2}$ and τ_π were 6 and 12 μs, and τ was 20 μs. The spectra were obtained at discrete frequency steps by integrating the spin echo. A Ag coil and resistor were used to reduce the Q and ensure that the Q was only weakly dependent on temperature. It was measured using a network analyzer. The spectra were corrected for the Q, mass, and Boltzmann factors.

The spectral intensity is also affected by the transverse relaxation time (T_2) that can depend on temperature as well as the fact that measurements cannot be made at $\tau=0$. Therefore, the spin-echo intensity was also measured as a function of τ and the magnetization $M(\tau)$ was extrapolated back to $\tau=0$ for a fixed pulse duration. In the HDHTSCs, $M(\tau)$ can be written as $M(\tau)=M_0\exp(-2\tau/T_{2R})\exp(-2\tau^2/T_{2g}^2)$. The first factor arises from the spin-lattice relaxation and it is known as the Redfield correction.[21] The second Gaussian

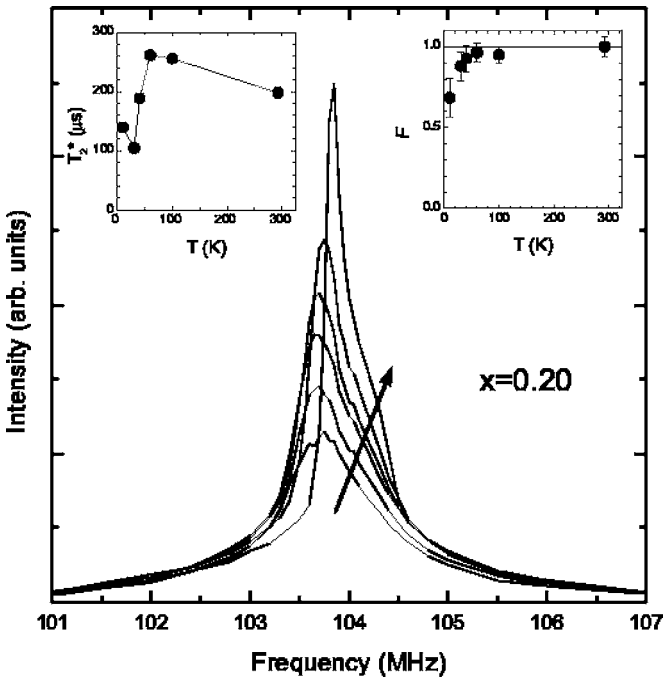

FIG. 1. Plot of the ^{63}Cu NMR spectra from a $Pr_{1.8}Ce_{0.2}CuO_4$ powder sample against frequency for an applied magnetic field of 9.2 T and at 10, 30, 40, 60, 100, and 294 K. The arrow indicates increasing temperature. The spectra were corrected for Q and the Boltzmann factor. Left inset: Plot of T_2^* against temperature measured at the peak frequency. Right inset: Plot of the integrated ^{63}Cu NMR intensity F against temperature after the T_2^* correction and normalized to the high-temperature value.

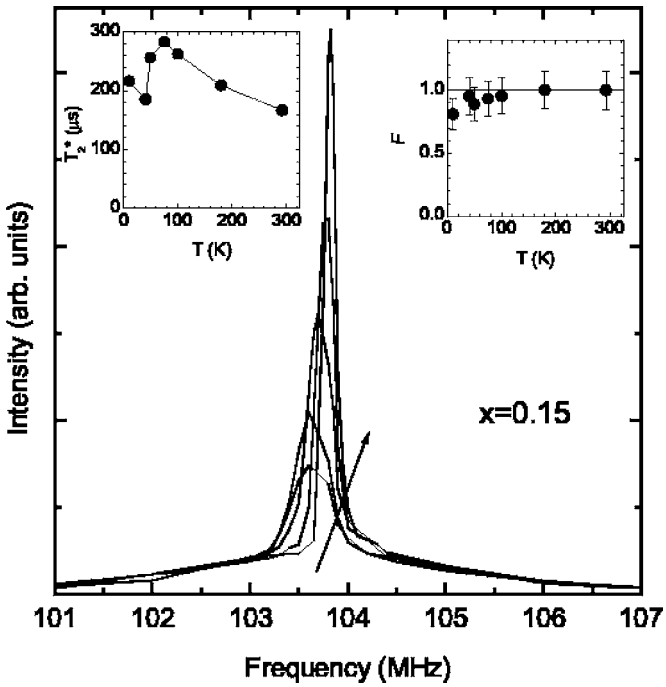

FIG. 2. Plot of the ^{63}Cu NMR spectra from a c-axis aligned $Pr_{1.85}Ce_{0.15}CuO_4$ with the ab plane parallel to the applied magnetic field of 9.2 T against frequency and at 10, 40, 100, 180, and 293 K. The spectra were corrected for Q and the Boltzmann factor. Left inset: Plot of T_2^* against temperature measured at the peak frequency. Right inset: Plot of the integrated ^{63}Cu NMR intensity F against temperature after the T_2^* correction and normalized to the high-temperature value.

factor arises from the electron-enhanced indirect nuclear spin-spin coupling between neighboring Cu nuclei.[22,23] This factor reduces to $\exp(-2\tau/T_2)$ in the absence of spin-spin coupling, if there are significant short-wavelength spatial inhomogeneities or if all the spins are not flipped by the excitation pulse. It has also been reported for temperatures near and below the temperature where the reduction in the Cu NMR intensity is observed in some of the HDHTSCs. It also occurs in $Sr_{0.9}La_{0.1}CuO_2$ and $Pr_{1.85}Ce_{0.15}CuO_4$ below 300 K. For this reason, the magnetization at $\tau=0$ was estimated by fitting the spin-echo intensity to $M(\tau)=M_0\exp(-2\tau/T_2^*)$, where $1/T_2^*=1/T_{2R}+1/T_2$.

The ^{63}Cu NMR spectra from the $Pr_{1.8}Ce_{0.2}CuO_4$ powder sample are plotted in Fig. 1 for temperatures increasing from 10 to 294 K. As noted previously, the spectra contain a narrow region that can be attributed to ^{63}Cu $1/2\leftrightarrow-1/2$ transitions from unoriented grains[19,24] and it is similar to that obtained from unoriented $Sr_{0.9}La_{0.1}CuO_2$.[18,25–27] For c-axis aligned samples, the peak for the ab plane parallel to the applied magnetic field occurs near 103.82 MHz and the peak for the c axis parallel to the applied magnetic field occurs near 104.4 MHz. This is consistent with previous measurements on aligned samples.[19] Since ^{63}Cu has a nuclear spin of $I=3/2$ and an appreciable nuclear quadrupole moment, two additional quadrupole peaks are expected. However, they are not observed in this compound or in the other EDHTSC, $Sr_{0.9}La_{0.1}CuO_2$.[18,25–27] It has been suggested that the electric-field gradient is small and charge disorder broadens the two expected quadrupole satellites.[18,19] Note that the ^{65}Cu NMR spectra occur at a higher frequency.

In this Brief Report, we are interested in the ^{63}Cu NMR intensity and it can be seen in Fig. 1 that there is a broadening of the spectra and a decrease in the absolute intensity. It has previously been shown that the broadening is due to Pr^{3+}, which is a van Vleck paramagnet.[19] To obtain the integrated intensity, it is important to measure T_2^* under the same excitation conditions with a $\tau_{\pi/2}$ of 6 μs. The resultant spin-spin relaxation data did not contain a Gaussian factor and could be fitted to $M(\tau)=M_0\exp(-2\tau/T_2^*)$, where the T_2^* data are plotted in the inset in Fig. 1 against the temperature. While this can occur because not all of the nuclear spins are flipped, we note that measurements on aligned samples with shorter $\tau_{\pi/2}$ pulse lengths also reveal the absence of a Gaussian component. Similar behavior is observed in $Sr_{0.9}La_{0.1}CuO_2$ for temperatures below 300 K. It can be seen in the left inset in Fig. 1 that T_2^* is a weak function of temperature down to 60 K. In all cases, T_2^* is above 100 μs and hence the T_2^* correction to the integrated ^{63}Cu NMR intensity is not large. This can be compared with $La_{2-x}Sr_xCuO_4$, where T_2^* can be below 20 μs.[2] The integrated ^{63}Cu NMR intensity is plotted in the right inset in Fig. 1. It is apparent that there is only a small decrease in the ^{63}Cu NMR intensity at low temperatures that could be due to supercurrent screening effects.

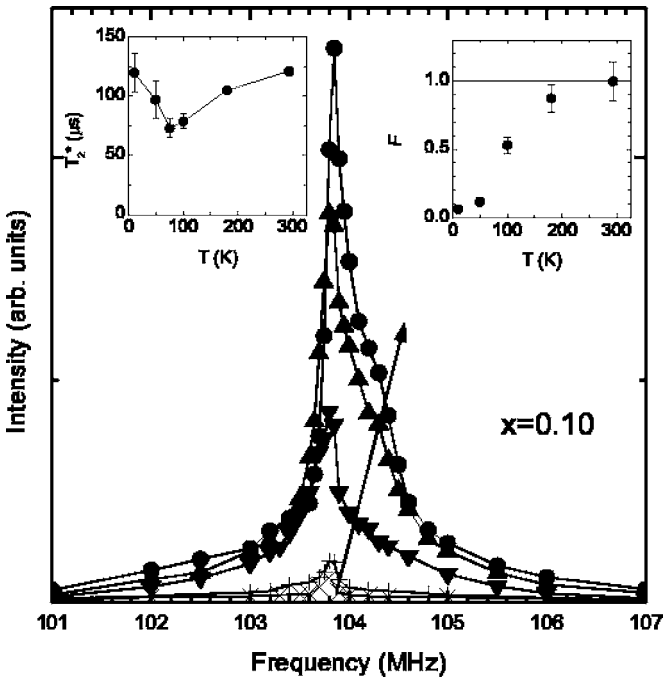

FIG. 3. Plot of the ^{63}Cu NMR spectra from a $Pr_{1.9}Ce_{0.1}CuO_4$ powder sample against frequency for an applied magnetic field of 9.2 T and at 10, 50, 100, 180, and 293 K. The arrow indicates increasing temperature. The spectra were corrected for Q and the Boltzmann factor. Left inset: Plot of T_2^* against temperature measured at the peak frequency. Right inset: Plot of the integrated ^{63}Cu NMR intensity F against temperature after the T_2^* correction and normalized to the high-temperature value.

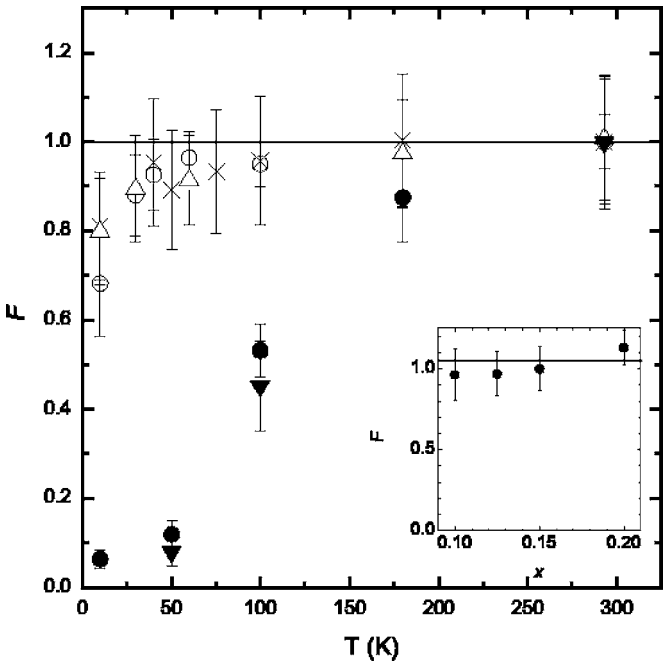

FIG. 4. Plot of the integrated ^{63}Cu NMR intensity F normalized to the high-temperature value against temperature for $Pr_{2-x}Ce_xCuO_4$ with $x=0.10$ (filled circles), $x=0.125$ (filled down triangles), $x=0.15$ (open up triangles), and $x=0.20$ (open circles). Also shown is the integrated intensity from a c-axis aligned $Pr_{1.85}Ce_{0.15}CuO_4$ with the ab plane parallel to the applied magnetic field (crosses). Inset: Plot of the integrated ^{63}Cu NMR intensity at 293 K against the Ce fraction and normalized to the $x=0.15$ value.

There is also no large decrease in the ^{63}Cu NMR intensity for $Pr_{1.85}Ce_{0.15}CuO_4$ that has a lower number of doped electrons per Cu. This can be seen in Fig. 2, where the ^{63}Cu spectra are plotted for a c-axis aligned sample and when the applied magnetic field is parallel to the ab plane. Previous measurements were done on unoriented powder samples.[18] The resultant ^{63}Cu NMR integrated intensity is plotted in the right inset in Fig. 2 after the T_2^* correction using the experimental data in the left inset in Fig. 2. There is only a small decrease in the integrated intensity at low temperatures that may be because of supercurrent shielding in the superconducting state.

However, it is clear in Fig. 3 that there is a large temperature-dependent decrease in the ^{63}Cu NMR intensity for $x=0.10$. Here, we plot the ^{63}Cu NMR spectra at different temperatures from a $Pr_{1.9}Ce_{0.1}CuO_4$ powder sample. The ^{63}Cu NMR spectrum at 293 K is similar to that seen in $Pr_{1.8}Ce_{0.2}CuO_4$. However, there is a rapid reduction in the ^{63}Cu NMR intensity with decreasing temperature. This cannot be attributed to a large decrease in T_2^*, as can be seen in the left inset in Fig. 3. There is a small decrease in T_2^* from 121 μs at 293 K to 73 μs at 75 K, and then T_2^* increases. The resultant ^{63}Cu NMR integrated intensity is plotted in the right inset in Fig. 3 after the T_2^* correction. It is apparent that the reduction occurs for temperatures below room temperature.

The ^{63}Cu NMR integrated intensity is plotted in Fig. 4 for all the samples after the small T_2^* correction. It is clear that there is a large temperature-dependent decrease in the ^{63}Cu NMR intensity starting below 293 K for $x=0.10$ and $x=0.125$. However, there is only a small or negligible decrease in the ^{63}Cu NMR intensity below T_c for $x=0.15-0.20$ that is probably due to supercurrent shielding effects.

While there is a clear reduction in the ^{63}Cu NMR intensity with decreasing temperature for $x\leqslant 0.125$, it is apparent in the inset in Fig. 4 that there is no reduction in the intensity at room temperature within the experimental uncertainty. Here, we plot the integrated ^{63}Cu NMR intensity at room temperature after correction for the mass, Q, Boltzmann factor, and T_2^*.

In conclusion, we observe a large temperature-dependent reduction in the ^{63}Cu NMR intensity in the $Pr_{2-x}Ce_xCuO_4$ family of EDHTSCs for $x\leqslant 0.125$ and below room temperature. The previous observation of a doping-dependent reduction in $Sr_{0.9}La_{0.1}CuO_2$ suggests that this reduction is intrinsic to the EDHTSCs. A temperature-dependent reduction in the ^{63}Cu NMR intensity has also been reported from measurements on $La_{2-x}Sr_xCuO_4$ and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ for low hole doping where the loss in intensity is significant for $x<0.13$. This shows that a symmetry exists between the

electron-doped and hole-doped superconducting phase diagrams. It should be noted that for both doping conditions, there are no changes in the Cu spin-lattice or spin-spin relaxation rates that can be associated with an onset of a NMR intensity reduction. Therefore, it is possible that the slowing down of the spin dynamics occurs inhomogeneously.

We acknowledge funding support from the New Zealand Marsden Fund, the Royal Society of New Zealand, the New Zealand Foundation for Research Science and Technology, and the European Commission NMP4-CT-2005-517039. We are grateful to B. Büüchner for access to the NMR facilities at the IFW, Dresden.

[1] A. W. Hunt, P. M. Singer, A. F. Cederström, and T. Imai, Phys. Rev. B **64**, 134525 (2001).
[2] M.-H. Julien *et al.*, Phys. Rev. B **63**, 144508 (2001).
[3] P. M. Singer and T. Imai, Phys. Rev. Lett. **88**, 187601 (2002).
[4] Y. Kobayashi *et al.*, J. Phys. Soc. Jpn. **70**, 1133 (2001).
[5] N. J. Curro, P. C. Hammel, B. J. Suh, M. Hucker, B. Buchner, U. Ammerahl, and A. Revcolevschi, Phys. Rev. Lett. **85**, 642 (2000).
[6] T. Sawa, M. Matsumura, and H. Yamagata, J. Phys. Soc. Jpn. **70**, 3503 (2001).
[7] P. M. Singer, A. W. Hunt, A. F. Cederström, and T. Imai, Phys. Rev. B **60**, 15345 (1999).
[8] G. B. Teitel'baum, I. M. Abu-Shiekah, O. Bakharev, H. B. Brom, and J. Zaanen, Phys. Rev. B **63**, 020507(R) (2000).
[9] M. Matsumura, T. Ikeda, and H. Yamagata, J. Phys. Soc. Jpn. **69**, 1023 (2000).
[10] A. W. Hunt, P. M. Singer, K. R. Thurber, and T. Imai, Phys. Rev. Lett. **82**, 4300 (1999).
[11] K. Yamada *et al.*, Phys. Rev. B **57**, 6165 (1998).
[12] J. M. Tranquada, J. D. Axe, N. Ichikawa, A. R. Moodenbaugh, Y. Nakamura, and S. Uchida, Phys. Rev. Lett. **78**, 338 (1997).
[13] H. A. Mook and P. Dai, Nature (London) **404**, 729 (2000).
[14] P. Dai, H. A. Mook, and F. Dogan, Phys. Rev. Lett. **80**, 1738 (1998).
[15] S. R. White and D. J. Scalapino, Phys. Rev. B **61**, 6320 (2000).
[16] V. J. Emery, S. A. Kivelson, and H. Q. Lin, Phys. Rev. Lett. **64**, 475 (1990).
[17] V. J. Emery, E. Fradkin, S. A. Kivelson, and T. C. Lubensky, Phys. Rev. Lett. **85**, 2160 (2000).
[18] G. V. M. Williams, J. Haase, M. S. Park, K. H. Kim, and S. I. Lee, Phys. Rev. B **72**, 212511 (2005).
[19] G. V. M. Williams, S. Krämer, R. Dupree, and A. Howes, Phys. Rev. B **69**, 134504 (2004).
[20] M. Brinkmann, T. Rex, H. Bach and K. Westerholt, Phys. Rev. Lett. **74**, 4927 (1995).
[21] R. L. Corey, N. J. Curro, K. Ohara, T. Imai, C. P. Slichter, K. Yoshimura, M. Katoh, and K. Kosuge, Phys. Rev. B **53**, 5907 (1996).
[22] C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39**, 274 (1989).
[23] C. H. Pennington and C. P. Slichter, Phys. Rev. Lett. **66**, 381 (1991).
[24] G. V. M. Williams *et al.*, Solid State Nucl. Magn. Reson. **26**, 236 (2004).
[25] T. Imai, C. P. Slichter, J. L. Cobb, and J. T. Markert, J. Phys. Chem. Solids **56**, 1921 (1995).
[26] K. Mikhalev *et al.*, Physica C **304**, 164 (1998).
[27] G. V. M. Williams, R. Dupree, A. Howes, S. Kramer, H. J. Trodahl, C. U. Jung, M. S. Park, and S. I. Lee, Phys. Rev. B **65**, 224520 (2002).