PHYSICAL REVIEW B **78**, 100503(R) (2008)

Pressure dependence of the oxygen isotope effect in the superconductor $YBa_2Cu_4O_8$

N. Suresh, J. G. Storey, G. V. M. Williams, and J. L. Tallon
MacDiarmid Institute, Industrial Research Ltd., P.O. Box 31310, Lower Hutt, New Zealand
(Received 22 November 2007; published 5 September 2008)

We have carried out measurements of the pressure dependence to 1.2 GPa of the oxygen isotope effect on T_c in the high-T_c superconductor $YBa_2Cu_4O_8$ using a clamp cell in a superconducting quantum interference device magnetometer. This compound lies close to, but just above, the 1/8th doping point where in $La_{2-x}Sr_xCuO_4$ marked anomalies in isotope effects occur. Both isotopes show the same very large pressure dependence of T_c with the result that the isotope exponent remains low (~0.08), increasing slowly with pressure. This is discussed in terms of stripes, a competing pseudogap, and fluctuations.

DOI: 10.1103/PhysRevB.78.100503 PACS number(s): 74.72.Bk, 74.62.Fj, 74.25.Bt

There is ongoing debate as to whether electron-phonon interactions play an important role in the physics of high-T_c superconductors and especially in the pairing interaction between carriers. The experimental situation remains ambiguous. An oxygen isotope effect has been observed in the $E(k)$ dispersion of $Bi_2Sr_2CaCu_2O_{8+\delta}$ using angle-resolved photoemission spectroscopy (ARPES).[1] Surprisingly, the isotope effect was observed at deeper energies outside the range of renormalization ("kink") effects near the Fermi level, E_F. These are difficult experiments especially given the resolution limits at that time. Recent higher-resolution studies[2] using laser ARPES indicate a more conventional scenario with the isotope effect only observed in the renormalization of the self–energy near E_F and a shift in the kink energy of about 3 meV. It is clear then that electron-phonon interactions are important in these systems but whether they contribute to pairing is another question.

In support of a minimal role, the isotope effect in T_c near optimal doping is found to be small,[3] and although it grows sharply with underdoping this is explicable in terms of the effect of a competing normal-state pseudogap reducing the order parameter toward zero while the spectral gap Δ remains finite.[4] With progressive underdoping this gives an increasing (diverging as $T_c \to 0$) isotope effect in T_c while that in Δ remains relatively unchanged. On the other hand Lee *et al.*[5] have observed a full oxygen isotope exponent in a peak in d^2I/dV^2 in scanning tunneling spectroscopy (STS) measurements when the spectra are referenced to the locally observed gap. In STS, local-gap referencing is important because the gap is found to be spatially variable due to some yet-to-be-established inhomogeneity. Lee *et al.*[5] have therefore identified a possible bosonic energy scale, Ω, for Eliashberg-type interactions with the electronic system that could be associated with pairing. The exponent $-\partial \ln \Omega / \partial \ln M$ was found to be close to 0.5, possibly indicating a pure phononic interaction.

There are further complications. First, around a hole concentration of $p=0.125$, at the so-called 1/8th point, there occurs a very marked anomaly in the isotope effects for both T_c (Refs. 6 and 7) and the superfluid density ρ_s (Ref. 7) in $La_{2-x}Sr_xCuO_4$. This reflects the presence of stripes[8] or perhaps a checkerboard structure[9] in which the spins and charges spatially separate and order. This results in a strong coupling of the electronic system to the lattice and a large resultant isotope effect, well above the canonical behavior expected for a competing pseudogap.[7]

Second, the underdoped cuprates exhibit a remarkably large pressure dependence of T_c that is yet to be fully understood.[10–12] One effect of pressure is to induce charge transfer, doping additional carriers into the conduction band. Pressure thus offers a mechanism to traverse the phase diagram.[12] In lightly underdoped cuprates $(0.125 < p < 0.16)$ it is found that $T_c(P)$ rises with pressure to a maximum, then falls.[12] Surprisingly, the maximum can be much greater than the value of $T_{c,\max}$ found at ambient pressure. For example, at ambient pressure $YBa_2Cu_4O_8$ has a large dT_c/dP coefficient of ≈ 5.5 K/GPa (Refs. 10 and 11), and T_c rises to a maximum of 108 K (Ref. 13) at somewhere between 9 and 12 GPa before falling at higher pressure. $Y_2Ba_4Cu_7O_{15-\delta}$, which is less underdoped, also has a large pressure coefficient[11] of $dT_c/dP=4.1$ K/GPa. On the other hand, for optimal and overdoped cuprates dT_c/dP is substantially reduced and becomes negative with overdoping.

These effects have been quantified by adapting the commonly used parabolic phase curve[14]

$$T_c(P) = T_{c,\max}(P)[1 - 82.6(p(P) - 0.16)^2], \qquad (1)$$

where both $T_{c,\max}$ and p are pressure dependent, and $dp/dP \approx 0.0055$ holes/Cu/GPa.[12] Such an analysis results in a value of $dT_{c,\max}/dP$ which is strongly pressure dependent, being very large in the lightly underdoped region (≥ 3 K/GPa), and becoming rather small in the overdoped region. However, the model clearly breaks down in the more underdoped region $(0.05 < p < 0.13)$, where $T_c(P)$ rises slowly with pressure and to a maximum, which little exceeds the ambient value.[12] The continued use of Eq. (1) in this region would require a large negative value of $dT_{c,\max}/dP$ and an abrupt crossover of $dT_{c,\max}/dP$ to large, positive values occurring close to $p=1/8$. Along with the anomalously large isotope exponent in the superfluid density[7] this is perhaps the clearest indication of a discontinuity in the phase diagram occurring near 1/8th doping. The uniaxial stress dependence of T_c in $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ single crystals using high-resolution thermal expansion measurements also shows a marked discontinuity at 1/8th doping.[15]

But this leads us to another problem. In the lightly underdoped region $T_{c,\max}$ has this unexpectedly large positive pressure coefficient. In contrast, the use of bond valence sums to characterize bond stresses leads to the conclusion that $T_{c,\max}$

 ©2008 The American Physical Society

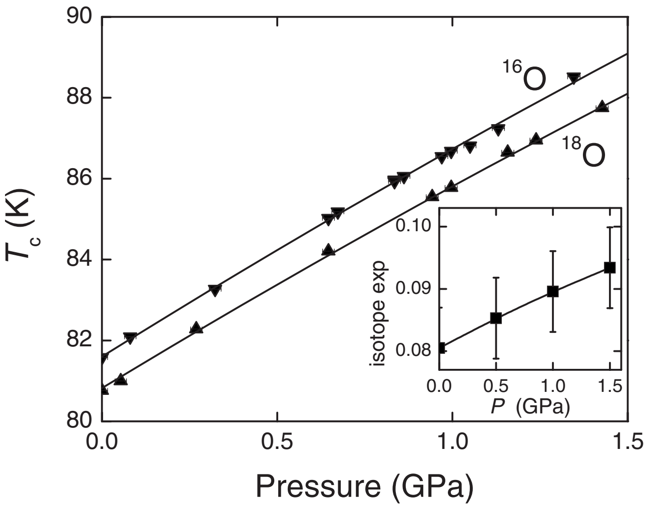

FIG. 1. The pressure dependence of T_c for $YBa_2Cu_4O_8$ with ^{16}O and ^{18}O oxygen isotope exchange. Inset: pressure dependence of the oxygen isotope exponent, $\alpha(T_c)=-\frac{M\times\Delta T_c}{\Delta M\times T_c}$.

has a negative pressure coefficient.[16,17] This is effectively confirmed across the series $RBa_2Cu_3O_{7-\delta}$, where as R is increased in size from Yb to La, $T_{c,\max}$ increases from 92 to 101 K by the ion size effect.[17] Based on these considerations the magnitude of $T_{c,\max}$ should decrease with pressure—it should have a negative pressure coefficient, while the opposite is observed. This contradiction is yet to be resolved.

There are thus anomalous pressure effects and anomalous isotope effects in underdoped cuprates. In the present work we bring these issues together to examine the pressure dependence of the oxygen isotope effect in $YBa_2Cu_4O_8$ (Y-124). We are motivated by the facts that (i) Y-124 lies very close to 1/8th doping with an estimated hole concentration of $p=0.13$. It is therefore likely to be influenced by stripe or checkerboard fluctuations if they are present in this system; (ii) Y-124 lies in the underdoped region where the pressure dependence of T_c is unusually high; (iii) it is sufficiently underdoped that the pseudogap plays a very important role in governing its thermodynamic and transport properties; (iv) it is rigidly oxygen stoichiometric and therefore oxygen isotope exchange, ensuring consistency of oxygen content and doping state, is straightforward; and (v) this material is one of the most defect-free cuprate superconductors known. Because of its rigid oxygen stability no oxygen ordering/disordering effects take place, either through changes in T or P. In the event, we find nothing too unexpected in the pressure dependence of the isotope effect. Both isotopic forms of Y-124 exhibit much the same large pressure coefficient. The result is that the isotope exponent remains small (≈ 0.08), rising only slowly with pressure.

Samples were prepared by standard solid-state reaction at 945 °C and 60 bar oxygen pressure as described previously.[4] A 12-mm diameter pellet was cut in half and one half was annealed in 98% ^{18}O and the other in pure ^{16}O using gold baskets placed in adjacent narrow fused quartz tubes. The samples were annealed at 760 °C for six hours at 0.95 bar pressure. The anneal was repeated four times with a new charge of isotopic O_2 gas each time. This resulted in a mass change in the ^{18}O sample consistent with 95% oxygen exchange. The nearly complete isotope exchange was confirmed by the shift in oxygen vibrational modes determined from Raman spectra.[4]

For each sample the superconducting transition temperature, T_c, was determined as a function of pressure in a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer using a miniature home-built piston clamp cell. The cell, with dimensions of 8.8-mm diameter and 65-mm length, was made from nonmagnetic Be-Cu (Mico Metal 97.75% Cu, 2% Be) with cobalt-free tungsten-carbide pistons (from Boride Products). The pistons are lightly tapered using electric-discharge machining.[18] The sample was loaded in a 2.67-mm diameter, 9-mm long, Teflon capsule along with Fluorinert FC70 and FC77 mixed in 1:1 ratio as a cryogenic hydrostatic pressure medium. A small piece of high purity Pb wire was included as a pressure calibrant. To apply pressure the cell was preloaded before clamping at room temperature using a laboratory press with calibrated digital pressure gauge (Ashcroft Model 2089, 0.05% accuracy). The pressure in the sample was measured from the reported shift in T_c of Pb at zero field.[19,20] In the course of this work we found that the pressure dependence of H_c had not been reported for Pb so we carried out an extensive investigation of $H_c(P,T)$ from which we determined the basic thermodynamic functions: the electronic entropy, specific heat coefficient, compressibility, and thermal expansion coefficient.[20]

Zero-field-cooled temperature sweeps were made at 2.5 mT to measure the diamagnetic magnetization and hence the onset of superconductivity. T_c values are plotted in Fig. 1 for the two isotope-exchanged Y-124 samples. The increase in T_c with pressure reveals a small quadratic curvature consistent with measurements over a much broader pressure range.[21] Quadratic fits gave the following results with $^{18}T_c(P)=80.82+5.25P-0.26P^2$ for the ^{18}O sample and $^{16}T_c(P)=81.60+5.40P-0.27P^2$ for the ^{16}O sample. The value of $dT_c/dP=5.40\pm0.15$ K/GPa in the latter case is similar to previous reports,[10,11,13] while the implicit value at $P=0$ of $\alpha\equiv -d\ln T_c/d\ln M=0.0805$ is also comparable to previous reports at ambient pressure.[4] Moreover, extrapolation of the quadratic fit results in a maximum T_c value of 108 K occurring at 10 GPa. This is very consistent with the values reported from diamond anvil studies at higher pressures.[21]

The inset to Fig. 1 shows the values of α deduced from the quadratic fits at four different pressures and corrected for the 95% isotope exchange. This shows only a small increase with pressure. How then are we to understand the anomalously high pressure coefficient in T_c, together with the small isotope exponent that grows only slightly with increasing pressure?

First, what is expected? Pressure generally transfers extra holes onto the CuO_2 planes.[12] Because the isotope effect is usually observed to decrease with increasing doping one might thus expect the isotope effect to decrease with pressure. Moreover, an increase in doping would tend to move the sample further away from 1/8th doping and hence away from any anomaly associated with stripe instability.[6] This also would tend to decrease the isotope effect.[7] More important, however, is the large pressure coefficient in T_c and this does not seem explicable in terms of a simple doping effect, requiring as it does an anomalously large value of $dT_{c,\max}/dP$ (and of opposite sign to what is expected).[16,17]

There is also the possibility that pressure enhances the tendency to stripe formation. $La_{2-x}Sr_xCuO_4$ is generally recognized to be the most inclined to stripe formation of the common high-T_c superconductors. Near $p=1/8$ this material exhibits a very large isotope effect in both T_c and in the superfluid density, ρ_s, departing severely from the canonical behavior expected for a pseudogap competing with superconductivity.[7] This indicates the strong coupling of the electronic system to the lattice in this region where stripe or checkerboard inhomogeneity occurs. Interestingly, $YBa_2Cu_3O_{7-\delta}$ (Y-123) remains on the canonical line of $\alpha(\rho_s)$ versus $\alpha(T_c)$ showing no apparent stripe-derived anomaly.[7] But we should not conclude from this that "stripe" correlations are irrelevant in Y-123 and Y-124. The $T_c(p)$ phase curve for $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ is almost identical to that for $La_{2-x}Sr_xCuO_4$ with the "60 K plateau" in Y-123 coinciding with the T_c anomaly in $La_{2-x}Sr_xCuO_4$ at 1/8th doping.[22] This feature in Y-123 is often thought to be associated with oxygen ("ortho-II") ordering but substitution of La for Ba, and Ca for Y shows that it is pinned to $p=1/8$, independent of oxygen content.[22] Interestingly, Y-124 (doped with La) also exhibits a 60 K plateau.[23] These features are almost certainly associated with short-range stripe correlations.

The CuO_2 planes in $La_{2-x}Sr_xCuO_4$ experience an in-plane compression in comparison with Y-123 and other higher T_c systems[16] resulting in a higher antiferromagnetic exchange interaction, J. If the shorter Cu-O bondlength and enhanced value of J is conducive to stripe formation near $p=0.125$ then this would explain the strong stripe tendency in $La_{2-x}Sr_xCuO_4$. Following this line of reasoning, the effect of pressure on Y-124 might be to enhance the tendency to stripe formation. Because it resides close to $p=0.125$ the increasing isotope exponent could signal an increasing tendency to stripe formation, even in this compound. But stripe development reduces T_c and, in this case, one would expect a negative pressure coefficient of T_c. In fact the opposite is found to be the case. Pressure suppresses stripes in $La_{2-x}Ba_xCuO_4$, narrowing the domain around $p=1/8$ in which T_c is diminished[24] and therefore resulting in a large positive value of dT_c/dP.

There is therefore a double anomaly. Correlation of compression effects across the cuprates, revealed for example using bond valence sums, would suggest that (i) $T_{c,\max}$ should be diminished by pressure, and (ii) stripes should be enhanced by pressure (which in turn would also tend to decrease T_c). Neither of these is true. What else might explain these results: this large pressure coefficient in T_c (for either isotope), leading to $T_{c,\max}$ as high as 108 K in Y-124? We consider two further possibilities: the role of (i) the pseudogap and (ii) fluctuations.

For underdoped and optimally doped samples the pseudogap competes with superconductivity, reducing T_c, ρ_s, the jump in specific heat at T_c, and the condensation energy. This causes an abrupt crossover from overdoped *strong superconductivity* to underdoped *weak superconductivity* at $p=p_{\rm crit}=0.19$ holes/Cu. A P-dependent rise in $T_{c,\max}$ could thus arise from a P-dependent decrease in the pseudogap (or alternatively a P-dependent shift of $p_{\rm crit}$ to lower doping). Unfortunately, studies on the effect of pressure on the pseudogap are inconclusive. Pressure effects on the relaxation rate of crystal-field excitations probed by inelastic neutron scattering suggest a weak reduction $dT^*/dP=-5.9\pm1.6$ K/GPa in the magnitude of the pseudogap temperature T^*.[25] Consistent with this, resistivity measurements on $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ suggest a decrease in T^* with pressure[26] but attributable wholly to P-induced changes in the doping state. On the other hand, hydrostatic pressure studies on the resistivity of $Hg_{0.82}Re_{0.18}Ba_2Ca_2Cu_3O_{8+\delta}$ revealed a positive coefficient $dT^*/dP=+7.4\pm0.6$ K/GPa.[27] Moreover, we feel that the inelastic neutron scattering data leaves many open questions. The background Korringa behavior lacks consistency with the pressure and doping dependence of the density of states and J. And, more importantly, these authors deduced that $T^*=55-60$ K, which seems far too low for a doping state of $p=0.15$. Hashimoto *et al.*[28] infer from ARPES studies that $T^*\approx140$ K for $La_{1.85}Sr_{0.15}CuO_4$.

Thus the experimental situation is inconclusive. However, we consider it unlikely that the pseudogap magnitude (at constant doping level) decreases with increasing pressure. The pseudogap has been fairly conclusively associated with short-range AF spin correlations.[29–31] An increase in pressure should increase the pseudogap energy scale, E_g, due to the pressure-induced increase in J.[32,33] We expect, therefore, that pressure effects on the pseudogap probably cannot account for the large positive value of dT_c/dP in underdoped cuprates.

This leaves us with fluctuations. It has been shown that Gaussian superconducting fluctuations are present over a broad range of temperatures extending above T_c, and are probably responsible[34,35] for the anomalous Nernst effect observed up to 100 K above T_c.[36] By simple entropy conservation these fluctuations are responsible for a significant reduction in T_c below the mean-field value, T_c^{mf}. Evidence for this has been derived from a detailed fluctuation analysis of the specific heat anomalies in Y-123 and $Bi_2Sr_2CaCu_2O_{8+\delta}$.[37] This reveals a $T_c^{mf}(p)$ which decreases monotonically as a function of doping, in contrast to the well-known parabolic $T_c(p)$ observed in the actual phase curve—the downturn at low doping being due to strong fluctuation effects. If so, then the effect of pressure on T_c is different from that on T_c^{mf}, which could even be of different sign. dT/dP may be large and positive due to a P-induced increase in the interlayer coupling, thus reducing the effect of fluctuations and raising T_c closer to the mean-field T_c value. In this scenario the pressure derivative would increase sharply with decreasing doping, as observed. On the other hand, the isotope effect in T_c would more likely take the value of the isotope effect in T_c^{mf} which, in turn, would take its value from the isotope effect in Δ, the superconducting energy gap. This could naturally explain our observation of a very strong pressure dependence of T_c and a weak pressure dependence of the isotope effect.

In summary, for $YBa_2Cu_4O_8$ we find a very strong pressure dependence of T_c for both ^{16}O and ^{18}O isotopes and a small pressure-induced increase in the oxygen isotope effect. These two effects are difficult to reconcile with simple pressure-induced charge transfer and bond compression, which increases the magnitude of J. We surmise that the effect of pressure is to reduce the Gaussian fluctuations, which depress T_c below its mean-field value.

[1] G.-H. Gweon, T. Sasagawa, S. Y. Zhou, J. Graf, H. Takagi, D.-H. Lee, and A. Lanzara, Nature (London) **430**, 187 (2004).

[2] J. F. Douglas, H. Iwasawa, Z. Sun, A. V. Fedorov, M. Ishikado, T. Saitoh, H. Eisaki, H. Bando, T. Iwase, A. Ino, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, T. Masui, S. Tajima, K. Fujita, S. Uchida, Y. Aiura, and D. S. Dessau, Nature (London) **446**, E5 (2007).

[3] J. R. Franck, in *Physical Properties of High Temperature Superconductors IV*, edited by D. M. Ginsberg (World Scientific, Singapore, 1994), p. 189.

[4] G. V. M. Williams, J. L. Tallon, J. W. Quilty, H. J. Trodahl, and N. E. Flower, Phys. Rev. Lett. **80**, 377 (1998).

[5] J. Lee, K. Fujita, K. McElroy, J. A. Slezak, M. Wang, Y. Aiura, H. Bando, M. Ishikado, T. Masui, J.-X. Zhu, A. V. Balatsky, H. Eisaki, S. Uchida, and J. C. Davis, Nature (London) **442**, 546 (2006).

[6] M. K. Crawford, M. N. Kunchur, W. E. Farneth, E. M. McCarron III, and S. J. Poon, Phys. Rev. B **41**, 282 (1990).

[7] J. L. Tallon, R. S. Islam, J. Storey, G. V. M. Williams, and J. R. Cooper, Phys. Rev. Lett. **94**, 237002 (2005).

[8] J. Tranquada, B. Sternlieb, J. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).

[9] K. McElroy, D.-H. Lee, J. E. Hoffman, K. M. Lang, J. Lee, E. W. Hudson, H. Eisaki, S. Uchida, and J. C. Davis, Phys. Rev. Lett. **94**, 197005 (2005).

[10] B. Bucher, J. Karpinski, E. Kaldis, and P. Wachter, Physica C **157**, 478 (1989).

[11] J. L. Tallon and J. Lusk, Physica C **167**, 236 (1990).

[12] J. S. Schilling, in *Handbook of High-Temperature Superconductivity: Theory and Experiment*, edited by J. R. Schrieffer (Springer, New York, 2007), p. 427.

[13] E. N. Van Eenige, R. Griessen, R. J. Wijngaarden, J. Karpinski, E. Kaldis, S. Rusieki, and E. Jilek, Physica C **168**, 482 (1990).

[14] M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu, and N. E. Flower, Physica C **176**, 95 (1991).

[15] C. Meingast, T. Wolf, M. Kläser, and G. Müller-Vogt, J. Low Temp. Phys. **105**, 1391 (1996).

[16] A. Mawdsley, J. L. Tallon, and M. R. Presland, Physica C **190**, 437 (1992).

[17] G. V. M. Williams and J. L. Tallon, Physica C **258**, 41 (1996).

[18] I. R. Walker, Rev. Sci. Instrum. **70**, 3402 (1999).

[19] A. Eiling and J. S. Schilling, J. Phys. F: Met. Phys. **11**, 623 (1981).

[20] N. Suresh and J. L. Tallon, Phys. Rev. B **75**, 174502 (2007).

[21] R. J. Wijngaarden, D. T. Jover, and R. Griessen, Physica B **265**, 128 (1999).

[22] J. L. Tallon, G. V. M. Williams, N. E. Flower, and C. Bernhard, Physica C **282-287**, 236 (1997).

[23] J. L. Tallon and G. M. V. Williams, J. Less-Common Met. **164-165**, 70 (1990).

[24] M. Ido, N. Yamada, M. Oda, Y. Segawa, N. Momono, A. Onodera, Y. Okajima, and K. Yamaya, Physica C **185-189**, 911 (1991).

[25] P. S. Häfliger, A. Podlesnyak, K. Conder, and A. Furrer, Europhys. Lett. **73**, 260 (2006).

[26] L. J. Shen, C. C. Lam, V. Anand, S. H. Li, and X. Jin, Physica C **341-348**, 929 (2000).

[27] E. V. L. de Mello, M. T. D. Orlando, J. L. González, E. S. Caixeiro, and E. Baggio-Saitovich, Phys. Rev. B **66**, 092504 (2002).

[28] M. Hashimoto, T. Yoshida, K. Tanaka, A. Fujimori, M. Okusawa, S. Wakimoto, K. Yamada, T. Kakeshita, H. Eisaki, and S. Uchida, Phys. Rev. B **75**, 140503(R) (2007).

[29] J. L. Tallon and J. W. Loram, Physica C **349**, 53 (2001).

[30] N. Harrison, R. D. McDonald, and J. Singleton, Phys. Rev. Lett. **99**, 206406 (2007).

[31] B. Kyung, Phys. Rev. B **64**, 104512 (2001).

[32] M. C. Aronson, S. B. Dierker, B. S. Dennis, S.-W. Cheong, and Z. Fisk, Phys. Rev. B **44**, 4657 (1991).

[33] A. A. Maksimov and I. I. Tartakovskii, J. Supercond. **7**, 439 (1994).

[34] I. Ussishkin, S. L. Sondhi, and D. A. Huse, Phys. Rev. Lett. **89**, 287001 (2002).

[35] I. Kokanovic, J. R. Cooper, and M. Matusiak, arXiv:0805.4293 (unpublished).

[36] Z. A. Xu, N. P. Ong, Y. Wang, T. Kakeshita, and S. Uchida, Nature (London) **406**, 486 (2000).

[37] J. L. Tallon, J. G. Storey, and J. W. Loram (unpublished).