Pressure dependence of the oxygen isotope effect in YBa$_2$Cu$_4$O$_8$

N. Suresh$^1$, J.G. Storey$^2$, G.V.M. Williams$^1$ and J.L. Tallon$^{1,2}$

$^1$MacDiarmid Institute, Industrial Research Ltd.,
P.O. Box 31310, Lower Hutt, New Zealand, and
$^2$School of Chemical and Physical Sciences, Victoria University, P.O. Box 600, Wellington, New Zealand.

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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$_2$Cu$_4$O$_8$ using a clamp cell in a SQUID magnetometer. This compound lies close to, but just above, the 1/8th doping point where in La$_{2-x}$Sr$_x$CuO$_4$ 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) but increases slightly with increasing pressure. This is discussed in terms of stripe suppression, a competing pseudogap and the effect of superconducting fluctuations.

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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$_2$Sr$_2$Cu$_2$O$_{8+δ}$ using angle resolved photoemission spectroscopy (ARPES). 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 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, and though it grows sharply with underdoping this is explicable in terms of the effect of a competing normal-state pseudogap reducing the order parameter towards zero while the spectral gap $\Delta$ remains finite. With progressive underdoping this gives an increasing (diverging as $T_c \to 0$) isotope effect in $T_c$ while that in $\Delta$ remains relatively unchanged. On the other hand Lee et al. 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. have therefore identified a possible bosonic energy scale, $\Omega$, for Eliashberg-like interactions with the electronic system that could be associated with the pairing. The exponent $-\partial \ln \Omega / \partial \ln M$ was found to be close to 0.5 indicating a pure phononic interaction.

There are further complications with high-$T_c$ superconductors (HTS). Firstly, 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 $T_{c,\text{max}}$ and the superfluid density $\rho_s^Z$ in La$_{2-x}$Sr$_x$CuO$_4$. This reflects the presence of stripes or perhaps a checkerboard structure 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.

Secondly, the underdoped cuprates exhibit a remarkably large pressure dependence of $T_c$ that is yet to be fully understood. 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. In lightly underdoped cuprates ($0.125 < p < 0.16$) it is found that $T_c(P)$ rises with pressure to a maximum then falls. Surprisingly, the maximum can be much greater than the value of $T_{c,\text{max}}$ found at ambient pressure. For example at ambient pressure YBa$_2$Cu$_4$O$_8$ has a large $dT_c/dP$ coefficient of $\approx 5.5$ K/GPa and $T_c$ rises to a maximum of 108 K at somewhere between 9 and 12 GPa before falling at higher pressure. Y$_2$Ba$_4$Cu$_4$O$_{15-\delta}$, which is less underdoped, also has a large pressure coefficient 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 adopting the commonly used parabolic phase curve:

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

where both $T_{c,\text{max}}$ and $p$ are pressure dependent, and $dp/dP \approx 0.0055$ holes/Cu/GPa. Such an analysis results in a value of $dT_{c,\text{max}}/dP$ which is strongly pressure dependent, being very large in the lightly underdoped region ($\geq 3$ 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. The continued use of equ. (i) in this region would require a large negative value of $dT_{c,\text{max}}/dP$ and an abrupt crossover of
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 HTS materials known. 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 dependence over the pressure range considered. The result is that the isotope exponent remains small ($\approx 0.08$) rising only very slowly (and perhaps not significantly) with $P$.

Samples were prepared by standard solid-state reaction at 945 °C and 60 bar oxygen pressure as described previously. 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 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 of $^{18}$O and $^{16}$O samples.

For each sample the superconducting transition temperature, $T_c$, was determined as a function of pressure in a Quantum Design MPMS 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 non-magnetic Be-Cu(Mico Metal 97.75% Cu, 2% Be) with cobalt-free tungsten-carbide pistons (from Boride). The pistons are lightly tapered using electric-discharge machining. 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.

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.

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 systems. The increase in $T_c$ with pressure reveals a small but clear quadratic curvature consistent with measurements over a much broader pressure range. Quadratic fits gave the following results with $^{18}T_c(P) = 80.82 + 5.25P - 0.26P^2$ for the $^{18}$O sample and $^{16}T_c(P) = 81.6 + 5.4P - 0.27P^2$ for the $^{16}$O sample. The value of $dT_c/dP = 5.4$ K/GPa in the

FIG. 1: The pressure dependence of $T_c$ for YBa$_2$Cu$_4$O$_8$ with $^{16}$O and $^{18}$O oxygen isotope exchange. Inset: pressure dependence of the oxygen isotope exponent, $\alpha(T_c) = \frac{-dT_c}{dT_c - \alpha(P)}$. The increase in $T_c$ with pressure reveals a small but clear quadratic curvature consistent with measurements over a much broader pressure range. Quadratic fits gave the following results with $^{18}T_c(P) = 80.82 + 5.25P - 0.26P^2$ for the $^{18}$O sample and $^{16}T_c(P) = 81.6 + 5.4P - 0.27P^2$ for the $^{16}$O sample. The value of $dT_c/dP = 5.4$ K/GPa in the

$dT_{c,max}/dP$ to large, positive values occurring close to $P=1/8$. Along with the anomalously large isotope exponent in the superfluid density, 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$_{1-\delta}$Ca$_\delta$)Ba$_2$Cu$_3$O$_{x}$ single crystals using high-resolution thermal expansion measurements also shows a marked discontinuity at 1/8th doping.

But this leads us to another problem. In the lightly underdoped region $T_{c,max}$ has this unexpectedly large positive pressure coefficient. The curious thing is that the use of bond valence sums to characterize bond stresses leads to the conclusion that $T_{c,max}$ has a negative pressure coefficient. This is effectively confirmed across the series RB$_2$Cu$_3$O$_{7-\delta}$ where, as R is increased in size from Yb to La, $T_{c,max}$ increases from 92K to 101K by the ion size effect. Based on these considerations the magnitude of $T_{c,max}$ should decrease with pressure - if it have a negative pressure coefficient, while the opposite is observed. This contradiction is yet to be resolved and it may need characterization of the pressure dependence of the competing pseudogap to progress our understanding of this issue - see below. In the absence of data on the pressure dependence of the pseudogap we will consider a further issue, the role of fluctuations and their response to pressure.

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$_2$Cu$_4$O$_8$ (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
latter case is similar to previous reports\textsuperscript{[10,11,14]} while the implicit value at $P = 0$ of $\alpha \equiv -\text{dln} T_c/\text{dln} M = 0.0805$ is also comparable to previous reports at ambient pressure\textsuperscript{4}. Moreover, extrapolation of the quadratic fit results in a maximum $T_c$ value of 108K occurring at 10 GPa. This is very consistent with the values reported from a collection of diamond anvil studies at higher pressures\textsuperscript{21}.

The inset to Fig. 1 shows the values of $\alpha$ deduced from the quadratic fits at four different pressures and corrected for the 95% isotope exchange. This shows only a small increase with pressure (which might, however, be statistically insignificant).

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?

Firstly, let us consider what might be expected. Pressure generally transfers extra holes onto the CuO$_2$ planes\textsuperscript{14}. 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 $1/8$th doping and hence away from any anomaly associated with stripe instability\textsuperscript{21}. This also would tend to decrease the isotope effect\textsuperscript{22}. For Y-124, however, these effects will be small because it already sits close to the plateau in $\alpha(p)$\textsuperscript{22}. More important 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)\textsuperscript{16,17,21}.

One has also to consider the possibility that the tendency to stripe formation is enhanced under pressure. La$_{2-x}$Sr$_x$CuO$_4$ 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, $\rho_s$, departing severely from the canonical behavior expected for a pseudogap competing with superconductivity\textsuperscript{7}. This indicates the strong coupling of the electronic system to the lattice in this region where stripe or checkerboard inhomogeneity occurs. Interestingly the Y-123 system remains on the canonical line of $\alpha(\rho_s)$ versus $\alpha(T_c)$ showing no apparent stripe-derived anomaly\textsuperscript{22}. 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,Ca)-123 is almost identical to that for La$_{2-x}$Sr$_x$CuO$_4$ with the “60K plateau” in Y-123 coinciding with the $T_c$ anomaly in La$_{2-x}$Sr$_x$CuO$_4$ at $1/8$th doping\textsuperscript{24}. This feature in Y-123 is often thought to be associated with oxygen (“orth-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\textsuperscript{25}. Interestingly, Y-124 (doped with La) also exhibits a 60K plateau\textsuperscript{24}. These features are almost certainly associated with short-range stripe correlations.

The CuO$_2$ planes in La$_{2-x}$Sr$_x$CuO$_4$ experience an in-plane compression in comparison with Y-123 and other higher $T_c$ systems\textsuperscript{15} 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$_{2-x}$X$_x$CuO$_4$. 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$_x$CuO$_4$, narrowing the domain around $p = 1/8$ in which $T_c$ is diminished\textsuperscript{22} and therefore resulting in a large positive value of $dT_c/dP$.

We are thus presented with 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. We probably, therefore, need to look to other possible effects to explain these results. What, for example, can explain the very large pressure coefficient in $T_c$ (for either isotope), leading to $T_{c,max}$ as high as 108K in Y-124. We consider two further possibilities: the role of (i) the pseudogap and (ii) fluctuations.

In the underdoped and optimally-doped regions the pseudogap competes with superconductivity, reducing $T_c$, $\rho_s$, the jump in specific heat at $T_c$ and the condensation energy, $U_0$. This causes an abrupt crossover from overdoped strong superconductivity to underdoped weak superconductivity at $p = p_{\text{crit}} = 0.19$ holes/Cu. A $P$-dependent rise in $T_{c,max}$ could thus be associated with a $P$-dependent decrease in the pseudogap (or alternatively a $P$-dependent shift of $p_{\text{crit}}$ to lower doping). We consider this to be unlikely in view of the fact that the pseudogap has been associated with short-range AF spin fluctuations\textsuperscript{26,27}. An increase in pressure should increase the pseudogap energy scale, $E_g$, hand in hand with the pressure-induced increase in $J_g$\textsuperscript{23}. Similarly, one would expect pressure to shift $p_{\text{crit}}$ to higher doping. These are ideas which we propose to test using pressure-dependent thermopower and Raman spectroscopy studies. However, as we have said - we expect that pressure effects on the pseudogap probably cannot account for the large positive value of $dT_c/dP$ in lightly underdoped cuprates.

This leaves us with fluctuations. In fact, we have formed the view that, in optimal and underdoped cuprates, Gaussian fluctuations are effective in significantly reducing $T_c$ below the mean-field value. Evidence for this has been derived from a detailed fluctuation analysis of the specific heat anomalies in YBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_x$Sr$_2$CaCu$_2$O$_{8+y}$\textsuperscript{30}. This leads to a monotonically decreasing mean-field transition temperature, $T_{c,\text{mf}}$, as a function of doping, along with the usual parabolic $T_c(p)$ - the downturn at low doping being due to strong fluc-
tuation effects. If so, then the effect of pressure may simply be to increase the interlayer coupling thus reducing the effect of fluctuations and raising $T_c$ closer to the mean-field $T_c$ value. The pressure derivative would increase sharply with decreasing doping, as observed. We intend to probe such effects by investigating the pressure-dependence of the fluctuation para-conductivity. The isotope effect would take the value of the isotope effect in the mean-field $T_{c}^{\text{mf}}$ value which in turn would take its value from the isotope effect in $\Delta$, 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 conclusion, for $\text{YBa}_2\text{Cu}_4\text{O}_8$ we find a very strong pressure dependence of $T_c$ for both $^{16}\text{O}$ and $^{18}\text{O}$ isotopes in combination with a zero, or 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. Some tests of this hypothesis are proposed.

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1. G.-H. Gweon, T. Sasagawa, S.Y. Zhou, J. Graf, H. Takagi, D.-H. Lee, A. Lanzara, Nature (London) 430, 187 (2004).
2. J.F. Douglas et al., Nature (London) 446, E5 (2007).
3. J.R. Franck, in Physical Properties of High Temperature Superconductors IV, ed. by D.M. Ginsberg (World Scientific, Singapore, 1994), p. 189.
4. G.V.M. Williams, J.L. Tallon, J. Quilty, H.J. Trodahl and N.E. Flower, Phys. Rev. Lett. 80, 377 (1998).
5. J. Lee et al., Nature (London) 442, 546 (2006).
6. M.K. Crawford, M.N. Kunchur, W.E. Farneth, E.M. McCarron III, 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 375, 561 (1995).
9. K. McElroy, D.-H. Lee, J.E. Hoffman, K.M. Lang, J. Lee, E.W. Hudson, H. Eisaki, S. Uchida, J.C. Davis, Phys. Rev. Lett. 94, 197005 (2005).
10. B. Bucher, J. Karpinski, E. Kaldis, P. Wachter, Physica C 157, 478 (1989).
11. J.L. Tallon and J. Lusk, Physica C 167, 235 (1990).
12. M.R. Presland, J.L. Tallon, R.G. Buckley, R.S. Liu and N.E. Flower, Physica C 176, 95 (1991).
13. J.S. Schilling, in Handbook of High-Temperature Superconductivity - Theory and Experiment, ed. by J.R. Schrieffer (Springer, New York, 2007), p. 427.
14. E.N. Van Eenige, R. Griessen, R.J. Wijngaarden, J. Karpinski, E. Kaldis, S. Rusiecki, E. Jilek, Physica C 168, 482 (1990).
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, J.L. Tallon, Physica C 258, 41 (1996).
18. I.R. Walker, Rev. Sci. Instrum. 70, 3402 (1999).
19. A. Elling and J.S. Schilling, J. Phys. F: Metal 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. D.J. Pringle, G.V.M. Williams and J.L. Tallon, Phys. Rev. B 62, 12527 (2000).
23. J.L. Tallon, G.V.M. Williams, N.E. Flower and C. Bernard, Physica C 282-287, 236 (1997).
24. J.L. Tallon and G.M.V. Williams, J. Less Common Metals 164-165, 70 (1990).
25. M. Ido, N. Yamada, M. Oda, Y. Segawa, N. Momono, A. Onodera, Y. Okajima and K. Yamaya, Physica C 185-189, 1158 (1991).
26. J.L. Tallon and J.W. Loram, Physica C 349, 53 (2001).
27. J.L. Tallon, J.W. Loram and C. Panagopoulos, J. Low Temp. Phys., 131 387 (2003).
28. M.C. Aronson, S.B. Dierker, B.S. Dennis, S-W.Cheong and Z.Fisk, Phys. Rev. B 44, 4657 (1991).
29. A.A. Maksimov and I.I. Tartakovskii, J. Supercon. 7, 439 (1994).
30. J.L. Tallon, J.G. Storey and J.W. Loram (unpublished).