Where is 99% of the condensation energy of $Tl_2Ba_2CuO_y$ coming from?

J. E. Hirsch$^a$ and F. Marsiglio$^b$

$^a$Department of Physics, University of California, San Diego, La Jolla, CA 92093-0319

$^b$Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G2J1

(Received November 15, 2021)

Anderson’s interlayer tunneling model can account for up to 1% of the condensation energy of $Tl_2Ba_2CuO_y$. Here we account for the remaining 99%. We predict an in-plane kinetic energy gain of 1 to 3 meV per planar oxygen when it goes superconducting. It is suggested that the effect may be most easily detected in underdoped dirty samples.

In conventional superconductors, the opening of the superconducting energy gap causes a reduction in optical absorption at low frequencies (below twice the gap value) \[1\], and this missing spectral weight is transferred to the zero-frequency \(\delta\)-function that determines the penetration depth \[2\] (so-called Ferrell-Glover-Tinkham (FGT) sum rule). It was proposed in Ref. 3 that in certain superconductors where pairing would arise from lowering of kinetic rather than of potential energy, the FGT sum rule would in appearance be violated, leading to the following novel phenomena: (1) a London penetration depth shorter than would be expected from the low frequency change in optical absorption and/or the normal state effective mass \[3\], and (2) a decrease in optical absorption at frequencies much higher than, and unrelated to, the superconducting energy gap, possibly near infrared or visible. Recent experimental observations by Basov and coworkers in several high \(T_c\) oxides \[4\] provide striking evidence for the existence of this physics in high \(T_c\) cuprates: for c-axis light polarization, the change in low frequency optical spectral weight accounts for just about 50% of the total spectral weight in the zero-frequency \(\delta\)-function, indicating that the remaining spectral weight comes from frequencies higher than the highest frequencies reached in the experiment, namely 150 meV. Note that this energy is about 6 times the value of the gap, within which all the optical spectral weight change should be contained according to conventional BCS theory \[5\]. These findings are also consistent with earlier experiments by Fugol et al \[6\] that report an anomalous decrease in optical absorption at frequencies in the visible range when high \(T_c\) samples become superconducting.

The well-known interlayer tunneling theory \[7\] (ILT) of the cuprates predicts a lowering of the c-axis kinetic energy as the system goes superconducting, so that the considerations of Ref. 3 apply to that model for the case when light is polarized along the c direction. Realizing this, Chakravarty \[8\] applied the analysis of Ref. 3 to the particular case of c-axis conductivity and found (not surprisingly) that a lowering of kinetic energy in that direction would be consistent with an apparent violation of the FGT sum rule for c-axis light polarization, and hence the phenomena discussed above. For planar light polarization instead, no apparent sum rule violation is expected within the ILT model.

However, within the ILT theory the kinetic energy lowering should entirely account for the condensation energy of the superconductor \[9\] \[10\]. In fact, in the analysis of c-axis transport of various high \(T_c\) oxides where agreement with ILT theory is claimed \[11\], e.g. \(La_{2-x}Sr_xCuO_4\), no distinction is made as to which frequency range in the optical absorption the \(\delta\)-function spectral weight is coming from: the entire weight is attributed to kinetic energy lowering, which in turn implies that ILT theory would also be consistent with observation of no sum rule violation \[11\]. However, the condensation energy of optimally doped $Tl_2Ba_2CuO_y$ (Tl2201) is estimated from specific heat measurements to be $80 \pm 100 \mu eV$ per CuO2 unit \[12\]. Even in the extreme case where the entire weight in the superfluid condensate would come from kinetic energy lowering the c-axis penetration depth required would be less than 2\(\mu m\) \[13\], which is significantly smaller than the measured penetration depth in that material, $\sim 17 \mu m$ \[14\] \[15\]. In other words, the measured penetration depth implies that the kinetic energy of c-axis motion in the superconducting state of $Tl_2Ba_2CuO_y$ accounts for less than 1% of its condensation energy \[16\] \[17\] \[18\] \[19\].

Still, we argue that Basov’s and Fugol’s experiments have clearly demonstrated that in high \(T_c\) materials at least some of the superconducting condensation energy originates in kinetic energy. It is then natural to ask whether the rest might too. If so, the remaining condensation energy should arise from lowering of the in-plane kinetic energy. However, Basov and coworkers report \[20\] no apparent sum rule violation in the in-plane response within experimental accuracy so far, approximately 10% \[10\].

This is however not surprising. We argue that the reason a sum rule violation has been detected in c-axis transport and not in in-plane transport so far is simply because...
the materials are in the dirty limit for c-axis conduction and close to the clean limit for in-plane conduction [17]. Note that the kinetic energy associated with the measured in-plane penetration depth of Tl2201 of \(\sim 2000\text{nm}\) is of order \(20-60\text{meV per CuO}_2\) unit, of which the condensation energy is only a tiny fraction. Still, as we discuss below, we expect that an in-plane sum rule violation will be detectable.

Within the model of hole superconductivity [18], pairing arises from lowering of kinetic energy in all directions when the system goes superconducting. Thus, the model predicts optical sum rule violation both in the in-plane and in the inter-plane response [3]. Because in-plane couplings are much larger than interplane ones, the bulk of the condensation energy in the model arises from kinetic energy lowering in the plane. Nevertheless, as we show in this paper, the model can readily account for the observed large sum rule violation in the c-direction and a much smaller sum rule violation in the plane, consistent with existing experimental results. It is predicted that with increased experimental accuracy an in-plane sum rule violation will be detected, most easily in the overdoped regime, which should readily account for the remaining 99% of the condensation energy in Tl2Ba2CuOy and other high \(T_c\) cuprates. In fact, the model predicts a lowering of kinetic energy that is much larger than the condensation energy, that is partially offset by an increase in potential energy.

Anderson remarks [9] that for several high \(T_c\) materials other than Tl2Ba2CuOy the condensation energy is completely accounted for by the lowering of the c-axis kinetic energy as determined from the c-axis penetration depth, and concludes that for those cases “this agreement effectively rules out any intralayer theory of high \(T_c\)”. This conclusion is logically flawed: the observations are entirely compatible with the existence of a much larger kinetic energy lowering from in-plane motion together with an increase in potential energy upon pairing, as predicted by our model.

The frequency-dependent conductivity in the superconducting state is given by \(\sigma_{\text{sf}}(\omega) = D\delta(\omega) + \sigma^{\text{reg}}_{\text{sf}}(\omega)\), with \(\sigma^{\text{reg}}_{\text{sf}}(\omega)\) the regular part. As discussed in Ref. 3, the superfluid weight in the zero-frequency \(\delta\)-function, \(D\), is given by

\[
D_\mu = \delta A^\mu_h + \delta A^\mu_a
\]

with \(\delta A^\mu_h\) the low frequency missing area, due to intra-band transitions, and

\[
\delta A^\mu_a = \frac{\pi e^2 a^2}{2h^2 v} [\langle -T^\mu_h >_s - \langle -T^\mu_h >_n]
\]

the missing area from much higher frequencies, related to interband transitions. \(\nu\) gives the volume of the unit cell, \(\mu\) indicates the direction of light polarization, and the right side of Eq. (2) gives the change in the carrier’s kinetic energy in the \(\mu\) direction as the system goes superconducting. The London penetration depth is given by \(\lambda_\mu = c/(8D_\mu)^{1/2}\), and an apparent sum rule violation exists if it is shorter than what is obtained from just the low frequency missing area, \(\delta A^\mu_h\), indicating the existence of \(\delta A^\mu_a\) even if it is not detected directly. The degree of sum rule ‘violation’ can be characterized by the parameter

\[
V_\mu = \frac{\delta A^\mu_h}{\delta A^\mu_a + \delta A^\mu_a}
\]

and was found by Basov et al to be approximately 0.5 in the \(c\) direction for several high \(T_c\) materials including \(\text{Tl}_2\text{Ba}_2\text{CuO}_y\).

For application to IFT theory the normal state kinetic energy in the \(c\) direction in Eq. (2) is assumed to be negligible, and Eq. (2) yields

\[
\frac{1}{\lambda^2_c} = \frac{4\pi e^2 d}{\hbar^2 c^2 a^2} < -T_c >_s
\]

with \(a\) and \(d\) in-plane and interplane lattice constants. The negative of the superconducting kinetic energy, \(< -T_c >_s\), is equated to the condensation energy, \(\epsilon_{\text{cond}}\). For the case of \(\text{Tl}_2\text{Ba}_2\text{CuO}_y\) \(\lambda_c \sim 17\text{\mu m}\), \(d = 11.6\text{\AA}\), \(a = 3.9\text{\AA}\), eq. (4) yields \(\epsilon_{\text{cond}} = 0.98\text{\mu eV per CuO}_2\) unit, two orders of magnitude smaller than the value estimated from specific heat measurements [3].

In the model of hole superconductivity, the kinetic energy in the \(\mu\) direction is given by [3]

\[
T^\mu = \sum_i [t_\mu + \Delta t_\mu (n_{i,-\sigma} + n_{i+\mu,-\sigma})] [\epsilon_{i\sigma}^\dagger c_{i+\mu,\sigma} + h.c.] = T^\mu + T^\Delta t
\]

with \(\epsilon_{i\sigma}^\dagger a\) a hole creation operator. The effective hopping in the \(\mu\) direction is given by

\[
t^\mu_{\text{eff}} = t_\mu + \Delta t_\mu n
\]

and it increases linearly with hole concentration \(n\). To a very good approximation [3] the change in kinetic energy Eq. (2) is simply given by the expectation value of the correlated hopping term

\[
\delta A^\mu_h = \frac{\pi e^2 a^2}{2h^2 v} < -T^{\Delta t} >_{s,a}
\]

where the subindex \(a\) indicates that only the anomalous expectation values are to be included [3].

In the clean limit at zero temperature we have simply

\[
\delta A^\mu_h = \frac{\pi e^2 a^2}{2h^2 v} < -T^{\Delta t} >_s
\]

where the average of the single particle kinetic energy includes also the ‘normal’ expectation values of the \(\Delta t\)
term, yielding the renormalized single particle hopping Eq. (6). The degree of sum rule violation in that case is given by

\[ V_\mu = \frac{< T_{\mu}^{\Delta t} >_{s,a}}{< T_{\mu}^t >_s + < T_{\mu}^{\Delta t} >_{s,a}}. \] (9)

The full Hamiltonian for the model includes in addition to the kinetic energy an on-site and nearest neighbor Coulomb repulsion:

\[ H_{\text{Coul}} = H_U + H_V = U \sum_i n_i^\uparrow n_i^\downarrow + V \sum_{<ij>} n_i n_j \] (10)

and the condensation energy of the superconductor is given by

\[ \epsilon_{\text{cond}} = [< T^t >_n - < T^t >_s] - < T^{\Delta t} >_{s,a} - < H_U >_{s,a} - < H_V >_{s,a} = \Delta t + \epsilon_{\Delta t} + \epsilon_U + \epsilon_V \] (11)

where the expectation values with subindex \( a \) indicate that only the anomalous contributions are to be included. In Eq. (11), a sum over the different directions is implicit for the terms that involve nearest neighbors. Quite generally, all contributions to \( \epsilon_{\text{cond}} \) other than \( \epsilon_{\Delta t} \) are negative: in the paired state, particles are closer together and experience larger Coulomb repulsion, and the single particle kinetic energy \( < T^t >_i \) is optimal (most negative) in the normal state. A positive \( \epsilon_{\text{cond}} \) originates from a large negative contribution from \( < T^{\Delta t} >_{s,a} \), i.e. a large kinetic energy lowering due to correlated hopping, which is to some extent compensated by the other terms in Eq. (11). In weak coupling, Eq. (11) is given by the usual form

\[ \epsilon_{\text{cond}} = \frac{\Delta_0^2}{2} N(\epsilon_F) \] (12)

with \( \Delta_0 \) the energy gap and \( N(\epsilon_F) \) the density of states at the Fermi energy.

In the model Eq. (5), each site denotes an oxygen atom in a Cu-O plane. Consider the following parameters to describe the CuO planes of Tl2201 (case 1): \( U = 5eV, t = 0.19eV, \Delta t = 0.29eV \). In the optimally doped case, with hole concentration \( n = 0.045 \) (per O atom), we obtain \( T_c = 85K \). Explicit calculation with the expressions given in Ref. 18 yields the results shown in Fig. 1. The sum rule violation parameter Eq. (9) is \( V_a = 3.4\% \) for the optimally doped case, well below the current experimental accuracy. It increases up to \( V_a = 6.5\% \) in the underdoped regime. As we will show below however, the resulting sum rule violation in the \( c \)-direction can be much larger, consistent with observations. The condensation energy per O atom is \( 53\mu eV \) in the optimally doped case, consistent with observations (\( \epsilon_{\text{cond}} \approx 100\mu eV \) per CuO2 unit). Note that it results from a much larger kinetic energy lowering due to correlated hopping, \( \epsilon_{\Delta t} = 1.2meV \), which is partially compensated by an increase in potential energy and in kinetic energy from single particle hopping.

The penetration depth in the ab plane in the clean limit is given by

\[ \frac{1}{\lambda_0^2} = \frac{4\pi e^2}{\hbar^2 c^2 d} [< -T_a^t >_s + < -T_a^{\Delta t} >_{s,a}]. \] (13)

For the optimally doped case, we find \( < -T_a^t >_s = -17.60meV \) and \( < -T_a^{\Delta t} >_s = -0.610meV \), and with \( d = 11.6\AA \) Eq. (13) yields \( \lambda_0 = 3697\AA \). However because there are other atoms between the CuO layers which are involved in the superconductivity it may be more appropriate to use \( d \sim 3\AA \) in Eq. (13), which then yields \( \lambda_0 = 1880\AA \), consistent with experimental observations \[13\]. Also, with the parameters chosen above, the density of states per CuO2 unit is \( N(\epsilon_F) = 1.25eV^{-1} \), consistent with experimental estimates for Tl2201.

Similarly, Fig. 2 shows results when a nearest neighbor repulsion is included (case 2). Here, \( U = 5eV, V = 0.65eV, t = 0.19eV, \) and \( \Delta t = 0.51eV \) is chosen to again yield \( T_c = 85K \) for the optimally doped case. Here the kinetic energy lowering is larger, and yields a sum rule violation \( V_a = 7.3\% \) for the optimally doped case which increases to \( V_a = 15\% \) in the underdoped regime. We expect the actual parameters describing Tl2201 to be somewhat in the range spanned by these two examples.
depth in the clean limit in the c direction is given by the smaller value of the parameter $\Delta t$ which would lead to an even larger effect.

What about the c direction? The simplest assumption is that $t$ and $\Delta t$ are reduced by the same factor. If we take $\lambda_c = 17\mu m$ from experiment, and assume in Eq. (4) that the c-axis kinetic energy lowering due to $\Delta t$ supplies 50% of the $\delta$-function weight, as found by Basov (i.e. 50% sum rule violation), we obtain $< T_c^\Delta > = 0.25\mu V$ (per O atom). For the parameters of case 1 above, we get an anisotropy factor

$$\frac{< T_{nc}^\Delta >}{< T_{nc}^\Delta >} = 2440$$

and the kinetic energy from single particle hopping scales approximately with the same factor. This corresponds to an anisotropy in hopping amplitudes (or effective masses) $t_a/t_c = m_a/m_c \sim 50$. The penetration depth in the clean limit in the c direction is given by

$$\frac{1}{(\lambda_{c\text{clean}})^2} = \frac{4\pi e^2 d}{\hbar^2 c^2 a^2} [< -T_c^\Delta > + < -T_c^\Delta >, s,a]$$

and yields $\lambda_{c\text{clean}} = 4.3\mu m$. The observed penetration depth in the c direction is however a factor of 4 larger, which we attribute to the effect of disorder reducing the contribution of $\delta A_t$ to the superfluid density, moving the system towards the dirty limit, thus increasing the violation parameter. In this connection it should also be noted that experimental results in the c direction show a faster variation of the violation parameter with doping than found in Figs. 1 and 2. This however is simply explained by the fact that the system is moving towards the clean limit with increased doping, as evidenced by the rapid increase in the optical conductivity, thus increasing the contribution of $\delta A_t$ faster than given by the results in Figs. 1 and 2. Quantitative fits will be discussed elsewhere.

In summary, the model of hole superconductivity predicted an apparent optical sum rule violation long before it was experimentally observed, which would be a manifestation of the reduction in effective mass and consequent lowering of kinetic energy that occurs upon

$$\frac{\hbar/\tau_a}{\hbar/\tau_c} = \frac{1}{1 + 1}$$

hence a larger scattering rate in the c direction will necessarily be associated with a larger sum rule violation in that direction.

As a further consistency check on the validity of this analysis we consider the normal state conductivities. For $\Delta_0 = 13meV$ as obtained from our model, the above analysis implies $\hbar/\tau_c = 5240cm^{-1}$. For in-plane transport instead, Puchkov et al find a scattering rate $1/\tau_a = 560cm^{-1}$, a factor of 10 smaller (which is consistent with a much smaller in-plane sum rule violation), and $\sigma_n(\omega \to 0) \sim 5000(\Omega cm)^{-1}$. Hence we expect in the c direction a conductivity that is smaller by a factor of approximately $\tau_a/\tau_c = m_c^*/m_a^* \sim 500$, i.e. $\sigma_a \sim 10(\Omega cm)^{-1}$ and frequency-independent over several times $\Delta_0$. This is consistent with observations.

Note that the c-axis kinetic energy lowering for these parameters is only 0.5% of the total condensation energy, and only 0.02% of the kinetic energy lowering originating in in-plane motion. Results for the other set of parameters discussed above are similar.

Will it be possible to observe a sum rule violation in the in-plane response? As shown above, the sum rule violation increases in the underdoped regime and hence it may be possible that the in-plane violation will be detected even if the system remains in the clean limit, especially if the nearest neighbor repulsion is appreciable (case 2 above). Furthermore, by introducing disorder, for example by ion irradiation, it may be possible to reduce the contribution of $\delta A_t$ to the superfluid density, moving the system towards the dirty limit, thus increasing the violation parameter. In this connection it should also be noted that experimental results in the c direction show a faster variation of the violation parameter with doping than found in Figs. 1 and 2. This however is simply explained by the fact that the system is moving towards the clean limit with increased doping, as evidenced by the rapid increase in the optical conductivity, thus increasing the contribution of $\delta A_t$ faster than given by the results in Figs. 1 and 2. Quantitative fits will be discussed elsewhere.
pairing. By assuming that Tl2201 is in the clean limit for in-plane conduction and in the dirty limit for the interplane response (which is consistent with observations \[17\]), we found that the model can explain experimental observations. In the optimally doped case, the kinetic energy lowering from c-axis motion accounts for \(\sim 1\%) of the condensation energy, and that of in-plane motion is 20-50 times larger than the condensation energy. In particular, the model can account for the 99\% condensation energy that is missing in the alternative proposed explanation of the sum rule violation experiments, the ILT model \[5\]. The fact that the predicted in-plane kinetic energy lowering is much larger than the condensation energy is fortunate and should allow for its experimental detection.

ACKNOWLEDGMENTS

The authors are grateful to D. Basov for stimulating discussion and for sharing his experimental results prior to publication. Hospitality of the Aspen Center for Physics where this work was started is gratefully acknowledged.

[1] R.E. Glover and M. Tinkham, Phys. Rev 108, 243 (1957).
[2] R.A. Ferrell and R.E. Glover, Phys. Rev 109, 1398 (1958); M. Tinkham and R.A. Ferrell, Phys.Rev.Lett. 2, 331 (1959).
[3] J. E. Hirsch, Physica C 199, 305 (1992); Physica C 201, 347 (1992).
[4] J. E. Hirsch and F. Marsiglio, Phys. Rev. B 45, 4807 (1992).
[5] D.N. Basov et al, Science 283, 49 (1999).
[6] I. Fugol et al, Sol.St.Comm. 86, 385 (1993).
[7] Z. Tesanovic, Phys. Rev. B 36, 2364 (1987); J.M. Wheatley, T.C. Hsu and P.W. Anderson, Nature 333, 121 (1988); Phys.Rev. B 37, 5897 (1988); P.W. Anderson, 'The Theory of Superconductivity in the High \(T_c\) cuprates”, Princeton University Press, Princeton, 1997.
[8] S. Chakravarty, Eur.Phys.J. B5, 337 (1998); S. Chakravarty, H.Y. Young and E. Abrahams, Phys.Rev.Lett. 82, 2366 (1999).
[9] P.W. Anderson, Science 268, 1154 (1995); Science 279, 1196 (1998).
[10] A.J. Leggett, Science 274, 587 (1996).
[11] A.A. Tsvelkov et al, Nature 395, 360 (1998).
[12] That is, the entire spectral weight in the \(\delta\)-function could come from low frequencies and the result would still be consistent with ILT theory as long as the weight in the \(\delta\)-function matched the condensation energy. Note that this implies in particular that ILT theory could not have predicted Basov’s observation of apparent sum rule violation.