Superconductivity by kinetic energy saving?

D. van der Marel, H. J. A. Molegraaf, C. Presura and I. Santoso

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D. VAN DER MAREL (`d.van.der.marel@phys.rug.nl`), H.
J. A. MOLEGRAAF (`h.j.a.molegraaf@phys.rug.nl`), C. PRESURA
(`cristian.presura@philips.com`) and I. SANTOSO (`i.santoso@student.rug.nl`)
*Materials Science Centre, University of Groningen, 9747 GA
Groningen, The Netherlands*

Abstract. A brief introduction is given in the generic microscopic framework of super-
conductivity. The consequences for the temperature dependence of the kinetic energy,
and the correlation energy are discussed for two cases: The BCS scenario and the non-
Fermi liquid scenario. A quantitative comparison is made between the BCS-prediction
for d-wave pairing in a band with nearest neighbor and next-nearest neighbor hoppping
and the experimental specific heat and the optical intraband spectral weight along the
plane. We show that the BCS-prediction produces the wrong sign for the kink at T_c of
the intraband spectral weight, even though the model calculation agrees well with the
specific heat.

1. Model independent properties of the superconducting state

1.1. INTERNAL ENERGY

When we cool down a superconductor below the critical temperature, the
material enters a qualitatively different state of matter, manifested by
quantum coherence over macroscopic distances. Because the critical tem-
perature represents a special point in the evolution of the internal energy
versus temperature, the internal energy departs from the temperature de-
pendence seen in the normal state when superconductivity occurs. Because
for $T < T_c$ the superconducting state is the stable equilibrium state, the
internal energy in equilibrium at $T = 0$ is an absolute minimum. Hence
cooling down from above the phase transition one would expect a drop in
the internal energy when at the critical temperature. This drop of internal
energy stabilizes the superconducting phase among all alternative states of
matter. An experimental example of this well known behavior is displayed
in Fig. 1.1, where the internal energy was calculated from the electronic
specific heat data(1) according to the relation $E_{int}(T) = \int_0^T c(T')dT'$. The
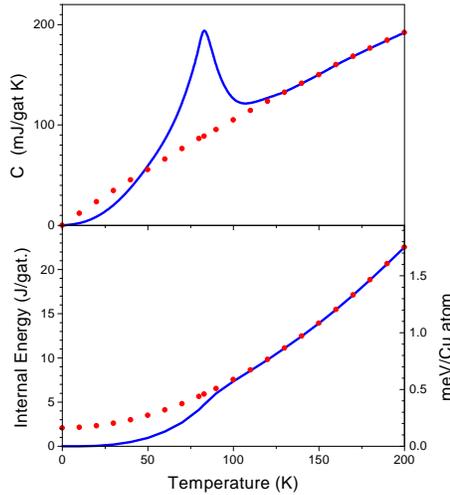broadened appearance of the phase transition suggests that the supercon-

Figure 1. Experimental internal energy and the specific heat obtained by Loram *et al*(1). The extrapolations are obtained following the procedure of Ref. (3)

ducting correlations disappear rather gradually when the temperature is increased above the phase transition, an effect which remains noticeable in the specific heat graph up to 125 K.

Understanding the mechanism of superconductivity means to understand what stabilizes the internal energy of the superconducting state. In BCS theory superconductivity arises as a result of a net attractive interaction between the quasi-particles of the normal state. Note, that implicitly this approach is firmly rooted in the paradigm of a Fermi-liquid type normal state. On the other hand, the school based on Anderson's original work(2) asserts, that a strong on-site *repulsive* interaction can also give rise to high T_c superconductivity. The latter models typically require that the material is not a Fermi liquid when superconductivity is muted, either by raising the temperature or by other means.

1.2. PAIR-CORRELATIONS

Without loss of generality, *i.e.* independent of the details of the mechanism which leads to superconductivity, it is possible to provide a microscopic definition of the superconducting state. For this purpose let us consider the correlation function defined as

$$G(r, R_1, R_2) = \left\langle \psi_\uparrow^\dagger(R_1 + r)\psi_\downarrow^\dagger(R_1)\psi_\downarrow(R_2)\psi_\uparrow(R_2 + r) \right\rangle \tag{1}$$

where $\psi_\sigma^\dagger(R_j)$ is a single electron creation operator. This function defines two types of correlation: (i) the electron pair-correlation as a function of the

relative coordinate $\vec{r}$, and (ii)v the correlation between two pairs located at center of mass coordinates $\vec{R}_1$ and $\vec{R}_2$. In the normal state there is no correlation of the phase of $G(r, R_1, R_2)$ over long distances $|R_1 - R_2|$ due to the finite mean free path of the electrons. As a result the integral over the center of mass coordinates of the correlation function

$$g(r) = \frac{1}{V^2} \int d^3 R_1 \int d^3 R_1 G(r, R_1, R_2) \tag{2}$$

averages to zero in the normal state. In contrast the superconducting state is characterized by long range phase coherence of the center of mass coordinates, implying (among other things) that the correlation function averaged over all center of mass coordinates, $g(r)$, is a finite number.

2. Internal energy and its decomposition using the BCS model

2.1. BCS: CORRELATION FUNCTION, AND CORRELATION ENERGY FOR D-WAVE PAIRING

In the weak coupling scenario of BCS theory the electrons have an effective attractive interaction, as a result of which they tend to form pairs. For the purpose of the present discussion we will assume that the interaction is of the form

$$H^i = V(r - r')\hat{n}(r)\hat{n}(r') \tag{3}$$

where $\hat{n}(r)$ is the electron density operator. The interaction energy in the superconducting state becomes lower than in the normal state, due to the fact that the effective attractive interaction favors a state with enhanced pair-correlations. The value of the interaction energy of the superconducting state, relative to the normal state is

$$\left\langle H^i \right\rangle_s - \left\langle H^i \right\rangle_n = \int d^3 r g(r) V(r) = \sum_k g_k V_k \tag{4}$$

where g_k and V_k are the Fourier transforms of $g(r)$ and $V(r)$ respectively. Using the Bogoliubov transformation the correlation function can be expressed(4) in terms of the gap-function Δ_k and the single particle energies $E_k = \{(\epsilon_k - \mu)^2 + \Delta_k^2\}^{1/2}$.

$$g_k = \sum_q \frac{\Delta_{q+k}\Delta_q^*}{4E_{q+k}E_q} \tag{5}$$

This corresponds to the conversion of a pair $(q, -q)$ to a pair with quantum numbers $(q+k, -q-k)$. In the expression for the correlation energy, Eq. 4, the transferred momentum k is carried by interaction kernel V_k.
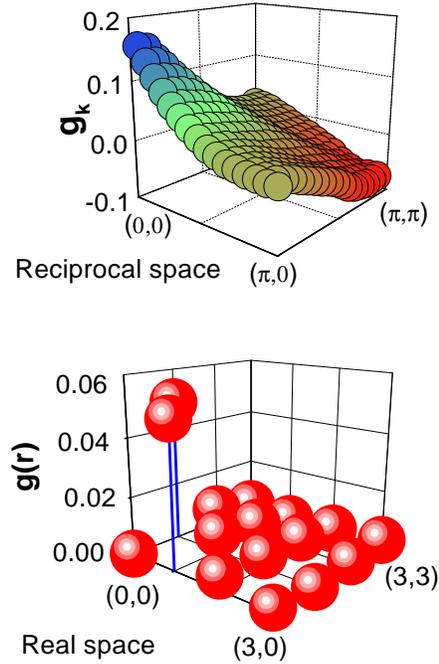
Figure 2. The k-space (top panel) and coordinate space (bottom panel) representation of the superconductivity induced change of pair-correlation function for d-wave symmetry (bottom panel). Parameters: $\Delta/W = 0.2$, $\omega_D/W = 0.2$. Doping level: x = 0.25

Starting from a model expression for the single electron energy-momentum dispersion ϵ_k, and the gap-function Δ_k, it is a straightforward numerical exercise to calculate the summations in Eq. 5. Adopting the nearest neighbor tight-binding model with a d-wave gap, and adopting the ratio $\Delta(\pi,0)/W = 0.2$, where W is the bandwidth, the correlation function g_k can be easily calculated, and the result is shown in Fig. 2.1. We see from this graph that a negative value of $\langle H^i \rangle_s - \langle H^i \rangle_n$ requires either (i) $V_k < 0$ for k in the neighborhood of the origin, or (ii) $V_k > 0$ for k in the vicinity of (π, π). The corresponding representation in real space, $g(r)$, shown in Fig. 2.1, illustrates that the dominant correlation of the d-wave superconducting state is of pairs where the two electrons occupy a nearest neighboring site, while the on-site amplitude is zero.

Combining the information of Fig. 2.1 with Eq. 2, it is clear that the strongest saving of correlation energy is expected if the electrons interact with an interaction of the form $V(r_1, r_2) = V_0 \sum_a \delta(\vec{r}_1 - \vec{r}_2 + \vec{a})$ where the vector a runs over nearest neighbor sites, and V_0 is a negative (meaning attractive) interaction between electrons on nearest neighbor sites.
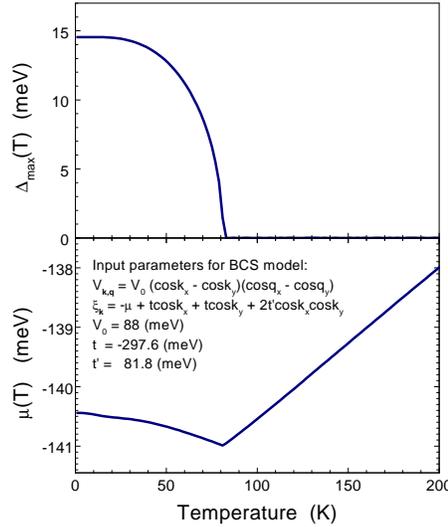
Figure 3. BCS prediction of the d-wave gap-function and the chemical potential. The parameters used for the calculation are indicated in the body of the Figure.

2.2. BCS: THE GAP-EQUATION, SPECIFIC HEAT AND INTERNAL ENERGY

To illustrate the predictions of BCS theory for the temperature dependence of the correlation energy and the kinetic energy, we start by solving the gap equation

$$\Delta_k = \sum_q \frac{V_{k-q}\Delta_q}{2E_q} \tanh\left(\frac{E_k}{2k_B T}\right) \qquad (6)$$

which must solved together with the constraint that the average number of particles is temperature independent. This requires that the chemical potential must be adjusted to keep the thermal average of $\sum_k \langle \hat{n}_k \rangle = N$ at a constant value. In the numerical examples of this paper we have adopted $N = 0.85$ corresponding to a hole doping of 0.15. This solution of the gap equation is shown in Fig. 2.2. Notice, that the temperature dependence of the chemical potential follows closely the experimental observations reported for Y123 in Ref. (7)

To check that the band-parameters used here are reasonable, we display in Fig. 2.2 the corresponding prediction for the specific heat and the internal energy. If we compare this to Fig. 1.1, we see that the band-parameters adopted here quantitatively reproduce the observed specific heat. Hence the present set of band-parameters (t,t') and the coupling parameter V_0 represent the best phenomenological choice for quantitative testing of the BCS-model.
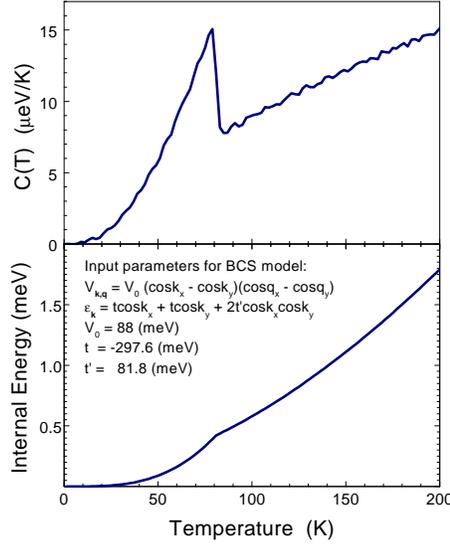
Figure 4. BCS prediction of the internal energy and the specific heat, using the parameters of Fig. 2.2

2.3. BCS: TEMPERATURE DEPENDENCE OF THE CORRELATION ENERGY AND THE KINETIC ENERGY

The BCS prediction for the temperature dependence of the average interaction energy follows from Eq. 4. We then use the BCS variational wave-function for the statistical average of Eq. 5, resulting in

$$\left\langle H^i \right\rangle_s - \left\langle H^i \right\rangle_n = -\sum_k \frac{|\Delta_k|^2}{2E_k} \tanh\left(\frac{E_k}{2k_B T}\right) \tag{7}$$

Simultaneously there is an increase of the 'kinetic' energy

$$\left\langle H^{kin} \right\rangle = \sum_k \epsilon_k \left\{ 1 - \frac{\epsilon_k - \mu}{E_k} \tanh\left(\frac{E_k}{2k_B T}\right) \right\} \tag{8}$$

In Fig. 2.3 this is displayed for the example of a d-wave order parameter.

3. Relationship between intra-band spectral weight and kinetic energy

A measure of the kinetic energy is provided by the following relation(8, 9, 10)

$$\int_{-\Omega}^{\Omega} d\omega \mathrm{Re}\sigma(\omega) d\omega = \pi \frac{e^2}{\hbar^2 V} \sum_{k,\sigma} \langle \hat{n}_{k,\sigma} \rangle \frac{\partial^2 \epsilon(\vec{k})}{\partial k^2} \tag{9}$$
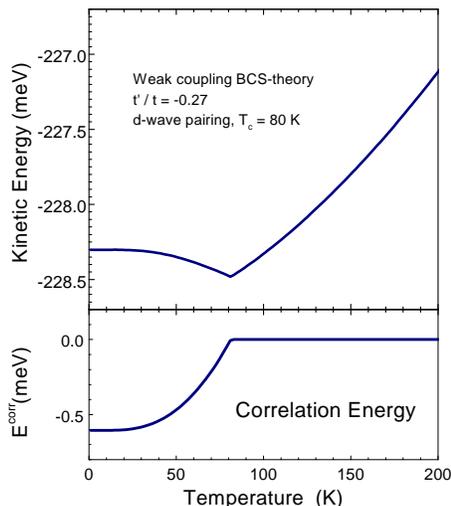
Figure 5. BCS prediction of the kinetic energy and the correlation energy.

where the high frequency limit indicates that the integral should include only the intra-valence band transitions, and the condensate peak at $\omega = 0$ if the material is a superconductor. The integral over negative and positive frequencies (note that $\sigma(\omega) = \sigma^*(-\omega)$) avoids ambiguity about the way the spectral weight in the condensate peak should be counted. If the band structure is described by a nearest neighbor tight-binding model, Eq. 9 leads to the simple relation

$$\rho_L \equiv \frac{\hbar^2}{a^2 \pi e^2} \int_{-\Omega}^{\Omega} \mathrm{Re}\,\sigma(\omega)d\omega = \langle -H_{kin} \rangle \qquad (10)$$

Hence in the nearest neighbor tight-binding limit the *partial* f-sum provides the *kinetic energy* contribution, which depends both on the number of particles and the hopping parameter $t(11, 12, 13, 14)$.

However, if the band-structure has both nearest neighbor hopping and next nearest neighbor hopping, Eq. 10 is not an exact relation, and instead Eq. 9 should be compared directly to the experiments. In Fig. 3 we compare the spectral weight, calculated directly using Eq. 9 to the result of Eq. 10. Note that the kinetic energy has to be divided by a factor two, as we are interested in the projection along one of the two axes in the ab-plane, which can be compared directly to the experimental value of ρ_L. From Fig. 3 we can conclude, that the effect of including t' in the calculation is rather small, and it is still OK to identify ρ_L with the kinetic energy apart from a minus sign.
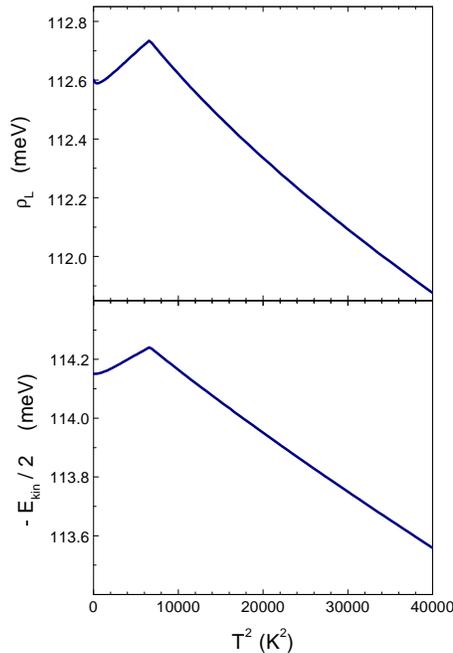
Figure 6. BCS prediction of the spectral weight function.

4. Experimental determination of the intra-band spectral weight

In two recent experimental papers measurements of ρ_L in Bi2212 have been reported (15, 16). The values of the kinetic energy change in the superconducting state were in quantitative agreement with each other, and both papers arrived at the same conclusion: Contrary to the BCS prediction, the kinetic energy of the superconducting state is *lower* than in the normal state (taking into account a correction for the temperature trends of the normal state). In Fig. 4 the data of Ref. (15) have been reproduced. Comparing this with the BCS prediction clearly demonstrates the large qualitative discrepancy between theory and experiment. Clearly the type of mechanism assumed in BCS theory is not at work here.

5. Implications of the experimental data

The trend seen in the experimental data has been predicted by Hirsch in 1992(17, 18, 19). The model assumption made by Hirsch was, that the hopping probability of a single hole between two sites becomes larger if one of the two sites is already occupied by a hole. Although this model provides good qualitative agreement with the optical experiments, it has one serious
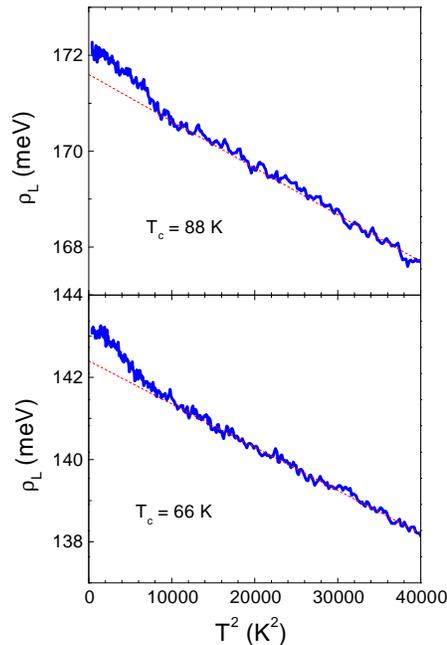
Figure 7. Experimental values of the ab-plane spectral weight function, taken from Ref. (15)

deficiency: It also predicts s-wave symmetry for the order parameter, in sharp contrast to a large body of experimental data which show that the superconducting gap in the cuprates has d-wave symmetry.

In a recent set of calculations based on the Hubbard model, Jarrell et al(20) obtained a similar effect as seen in our experiments, both for underdoped and optimally doped samples. Crudely speaking the mechanism is believed due to the frustrated motion of single carriers in a background with short-range (RVB-type) spin-correlations, which is released once pairs are formed.

6. conclusions

We have made a quantitative comparison between the BCS-prediction for d-wave pairing in a band with nearest neighbor and next-nearest neighbor hoppping and various experiments, in particular specific heat and measurements of the optical ab-plane sumrule. We have shown that the BCS-prediction produces the wrong sign for the kink at T_c of the ab-plane intraband spectral weight, while the model calculation is in good agreement with the experimental specific heat data.

Acknowledgements

References

1. J. W. Loram, J. Luo, J. R. Cooper, W. Y. Liang and J. L. Tallon, J. Physics and Chemistry of Solids **62**, 59-64 (2001).
2. P.W. Anderson, Science **235**, 1196 (1987).
3. D. van der Marel, A.J. Leggett, J.W. Loram, J.R. Kirtley Physical Review B Rapid Communications **66**, 140501R (2002).
4. There is an additional term, due to the fact that the chemical potential of the superconducting state is slightly shifted relative to the normal state(5, 6): $0.25 \sum_p |v_{p+k} v_p|^2$. In the numerical examples in this paper this additional term has been taken into account. Since the effect is small, we will not discuss it further here.
5. D. van der Marel, Physica C **165** (1990) 35-43;
6. D. van der Marel, and G. Rietveld, Phys. Rev. Lett. **69** (1992) 2575-2577;
7. G. Rietveld, N. Y. Chen, D. van der Marel, Phys. Rev. Lett. **69** (1992) 2578-2581;
8. M. R. Norman, and C. Pepin, Phys. Rev. B **66**, 100506(R) (2002).
9. R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
10. H. D. Drew, P. Coleman, Phys. Rev. Lett. **78**, 1572 (1997).
11. Pierre F. Maldague, Phys. Rev. **16**, 2437 (1977).
12. J. Carmelo and D. Baeriswyl, Phys. Rev. B **37**, 7541 (1988).
13. D. N. Basov, S. I. Woods, A. S. Katz, E. J. Singley, R. C. Dynes, M. Xu, D. G. Hinks, C. C. Homes, M. Strongin, Science **283**, 49 (1999).
14. S. Chakravarty, H. Kee, E. Abrahams, Phys. Rev. Lett. **82** , 2366 (1999).
15. H. J. A. Molegraaf, C. Presura, D. van der Marel, P. H. Kes , M. Li, Science **295**, 2239 (2002).
16. A.F. Santander-Syro, R.P.S.M. Lobo, N. Bontemps, Z. Konstantinovic, Z.Z. Li, H. Raffy, cond-mat/0111539 (2002).
17. J. E. Hirsch, Physica C **199**, 305 (1992).
18. J. E. Hirsch, Physica C **201** (1992) 347.
19. J. E. Hirsch, and F. Marsiglio, Physica C **331** (1999), 150-156.
20. Th. A. Maier, M. Jarrell, A. Macridin, C. Slezak, cond-mat/0211298 (2002).