PHYSICA C

Apparent violation of the conductivity sum rule in certain superconductors

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It is pointed out that the Ferrell–Glover–Tinkham sum rule relating the "missing area" in the low frequency conductivity to the penetration depth can be violated in certain superconductors. Its breakdown indicates that the effective mass of the carriers changes in entering the superconducting state, and implies a change in the conductivity at frequencies much higher than the superconducting gap, possibly near infrared or visible. The model of hole superconductivity predicts the occurrence of this phenomenon.

The conductivity sum rule [1] for a system of N_e electrons in a solid,

$$\int_0^\infty d\omega\, \sigma_1(q, \omega) = \frac{\pi e^2 N_e}{2m},\qquad (1)$$

is expected to hold quite generally, for arbitrary temperature and wavevector q, provided the integral is carried out to infinite frequency. Here, the mass m is the *bare* electron mass. This rule is anchored in basic principles of quantum mechanics and expresses the physical fact that at sufficiently high energies electrons will be insensitive to both electron–ion and electron–electron interactions and respond as free particles.

In the early days of BCS theory it was noted [2] that the opening of the superconducting energy gap would reduce the optical absorption at frequencies below twice the value of the gap (corresponding to far infrared or microwave frequencies). To preserve the sum rule eq. (1), Ferrell, Glover and Tinkham (FGT) [3] proposed that this "missing area" in the infrared conductivity would show up as a δ-function at zero frequency. In the superconducting state,

$$\sigma_{1s}(\omega) = D\delta(\omega) + \sigma_{1s}^{reg}(\omega)\qquad (2)$$

with the weight D determined by the sum rule eq. (1):

$$D = \int_{0^+}^\infty d\omega\, [\sigma_{1n}(\omega) - \sigma_{1s}(\omega)] \equiv \delta A,\qquad (3)$$

where the indices n and s denote normal and superconducting state, and δA is the "missing area". A Kramers–Kronig relation implies [3] that the δ-function contribution to σ_{1s} gives rise to a $1/\omega$ contribution to the imaginary part of the conductivity $(\sigma_{2s}(\omega) = 2D/\pi\omega)$, or equivalently to a London kernel

$$K_L = \frac{8D}{c^2} = \frac{1}{\lambda_L^2},\qquad (4)$$

with λ_L the London penetration depth. This expresses the physical fact that a lossless response implies perfect diamagnetism. Thus, from eqs. (3) and (4) it was argued that the missing area at low frequencies that occurs due to the opening of the superconducting energy gap provides an independent measurement of the penetration depth. Such a "consistency check" is still used nowadays by experimentalists [4] as a test on the validity of independently measured infrared conductivity and penetration depth.

The purpose of this paper is to point out that this argument (in a strict sense) does not hold in a certain class of superconductors, and that its breakdown leads to a novel experimental prediction: the

optical conductivity will be modified at frequencies far above the energy scale set by the superconducting energy gap when such a superconductor enters into a superconducting state.

Consider a single band tight binding model with electron kinetic energy

$$T = - \sum_{i,j} t_{ij}^{\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{h.c.}) = \sum_{\delta} T_{\delta} , \qquad (5)$$

where $c_{i\sigma}^{\dagger}$ creates an electron of spin σ at Wannier orbital i. We assume for simplicity nearest neighbor hopping only, in directions denoted by δ. A "partial" conductivity sum rule can be derived by restricting the Hilbert space to the states in this band and yields [5]:

$$\int_{0}^{\omega_m} d\omega \, \sigma_1^{\delta\delta}(q, \omega) = \frac{\pi e^2 a_{\delta}^2}{2\hbar^2} \langle -T_{\delta} \rangle . \qquad (6)$$

Here, $\langle \ \rangle$ denotes expectation value and ω_m is a high-frequency cutoff that is above all optical transitions involving states in this band but excludes transitions to other bands. a_{δ} is the lattice spacing in direction δ. For an almost empty band at zero temperature and in the absence of electron–electron interactions, eq. (6) reduces to eq. (1), with m replaced by the band mass m^*. Similarly for an almost full band one also obtains eq. (1), with N_e replaced by the number of holes; note, however, that the full sum rule eq. (1) is *not* particle–hole symmetric. Note also that in general the right-hand side of eq. (6) will depend on the interactions in the system as well as on temperature.

The FGT argument using the sum rule eq. (6) now leads to

$$D = \delta A_1 + \frac{\pi e^2 a_{\delta}^2}{2\hbar^2} [\langle -T_{\delta} \rangle_s - \langle -T_{\delta} \rangle_n] , \qquad (7)$$

where we denote by δA_1 the missing area for frequencies involving only states in this band:

$$\delta A_1 = \int_{0+}^{\omega_m} d\omega [\sigma_{1n}(\omega) - \sigma_{1s}(\omega)] . \qquad (8)$$

In general $\hbar\omega_m$ will be much larger than the superconducting energy gap. In the usual experimental setups the maximum frequency is restricted to a few times the energy gap, where σ_{1n} and σ_{1s} have become

equal. Thus, the "missing area" corresponds to the one given by eq. (8). Equation (7) then indicates that if there is an appreciable change in the carrier kinetic energy on entering the superconducting state, the assumed connection between low-frequency missing area and penetration depth or low-frequency $\sigma_{2s}(\omega)$ breaks down. Such a change will occur in systems where the effective mass of the carriers is different in the normal and superconducting states.

Conversely, if it is experimentally determined that the penetration depth disagrees with the value expected from the low-frequency missing area, the global sum rule eq. (1) indicates that there is missing (or excess) area somewhere else:

$$\delta A_h = D - \delta A_1 \qquad (9)$$

with $D = c^2 / (8\lambda_L^2)$ and

$$\delta A_h = \int_{\omega_m}^{\infty} d\omega [\sigma_{1n}(\omega) - \sigma_{1s}(\omega)] . \qquad (10)$$

This "high-frequency" missing area should occur at energies involving transitions to other bands, i.e. of order of at least fractions of eV in general. From eq. (7),

$$\delta A_h = \frac{\pi e^2 a_{\delta}^2}{2\hbar^2} [\langle -T_{\delta} \rangle_s - \langle -T_{\delta} \rangle_n] , \qquad (11)$$

so that its existence indicates that the carriers change their kinetic energy on entering the superconducting state. Figure 1 shows schematically the expected behavior of the real part of the conductivity in the normal and superconducting states, as well as the two
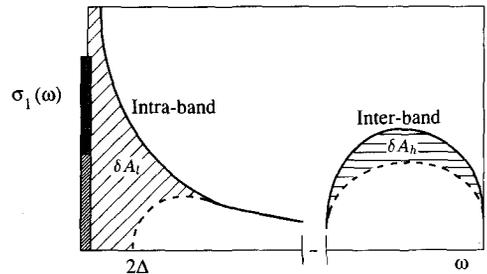

Fig. 1. Real part of the conductivity in the normal (solid lines) and superconducting (dashed lines) states (schematic). The missing areas from intra-band (δA_1, diagonally hatched) and inter-band (δA_h, horizontally hatched) transitions are shown as separate contributions to the δ-function at zero frequency.

contributions to the δ-function at zero frequency.

In the model of hole superconductivity [6] pairing is driven by the gain in kinetic energy that occurs when two holes are nearby. The kinetic energy for holes is given by eq. (5), with $c_{i\sigma}^\dagger$ a *hole* creation operator, and

$$t_{ij}^\sigma = t_{ij} + (\Delta t)_{ij}(n_{i,-\sigma} + n_{j,-\sigma}),\qquad (12)$$

with $n_{i,\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. The second term in this equation gives rise to a four-fermion operator term, i.e. an interaction, in eq. (5). Nevertheless it is easily verified that the proof [5] of the sum rule eq. (6) goes through unchanged when the hopping amplitude has the operator dependence given by eq. (12). The following treatment parallels the analysis of the London penetration depth in this model given in ref. [7].

Denoting by t_h and Δt the amplitudes t_{ij} and $(\Delta t)_{ij}$ between nearest neighbors, the average kinetic energy is given by

$$\langle T_\delta \rangle = -(t_h + n\Delta t) \sum_{i,\sigma} \langle c_{i+\delta,\sigma}^\dagger c_{i\sigma} + \text{h.c.} \rangle$$

$$-2\Delta t \sum_{i,\sigma} [\langle c_{i\sigma}^\dagger c_{i,-\sigma}^\dagger \rangle \langle c_{i,-\sigma} c_{i+\delta,\sigma} \rangle + \text{h.c}]$$

$$\equiv \langle T_\delta^t \rangle + \langle T_\delta^{\Delta t} \rangle,\qquad (13)$$

within a Hartree–Fock decoupling. This expression is in fact exact in the low density limit. The density-dependent correction to the hopping t_h in the first term in eq. (13) (n is the number of holes per site) arises from the "normal" Hartree–Fock decoupling of the interaction term. The "anomalous" expectation values in the second term in eq. (13) are of course only non-zero in the superconducting state.

Equation (11) yields for the "high frequency" missing area

$$\delta A_h = \frac{\pi e^2 a_\delta^2}{2\hbar^2} [\langle -T_\delta^t \rangle_s - \langle -T_\delta^t \rangle_n]$$

$$+ \frac{\pi e^2 a_\delta^2}{2\hbar^2} \langle -T_\delta^{\Delta t} \rangle.\qquad (14)$$

Explicit calculation shows that the single-particle contribution to the kinetic energy is essentially unchanged in going into the superconducting state. Thus, δA_h is given by the "anomalous" contribution to the kinetic energy expectation value, $\langle T_\delta^{\Delta t} \rangle$.

The "low-frequency" missing area is given by

$$\delta A_l = \frac{c^2}{8} K_{1\delta}^t + \frac{\pi e^2 a_\delta^2}{2\hbar^2} \langle -T_\delta^t \rangle_n,\qquad (15)$$

where $K_{1\delta}^t$ is the paramagnetic London kernel arising from the real part of the current–current correlation function. In the clean limit it is given by [7]

$$K_{1\delta} = \frac{32\pi e^2 a_\delta^2 (t_h + n\Delta t)^2}{\hbar^2 c^2} \sum_k \sin^2 k_\delta \left(\frac{\partial f}{\partial E_k}\right),\qquad (16)$$

with E_k the quasi-particle energy and f the Fermi function. As $T \to 0$ it goes to zero, while for $T \ge T_c$ it exactly cancels the kinetic energy expectation value in eq. (15).

Finally the expectation values in eq. (13) are given by

$$\langle T_\delta^t \rangle = -2(t_h + n\Delta t) \sum_k \cos k_\delta$$

$$\times \left(1 - \frac{\epsilon_k - \mu}{E_k}(1 - 2f(E_k))\right),\qquad (17a)$$

$$\langle T_\delta^{\Delta t} \rangle = -\frac{4\Delta t}{N} \sum_{kk'} (\cos k_\delta + \cos k_\delta') \frac{\Delta_k}{2E_k} \frac{\Delta_{k'}}{2E_{k'}}$$

$$\times (1 - 2f(E_k))(1 - 2f(E_{k'})),\qquad (17b)$$

with ϵ_k the band energy (with hopping $(t_h + n\Delta t)$), Δ_k the usual BCS gap function, μ the chemical potential and N the number of lattice sites.

There is a range of parameters in the model of hole superconductivity that give rise to properties that appear to be in agreement with various experimental observations in high-T_c oxides [6]. For illustration we consider here a two-dimensional model, with parameters

$$U = 5 \text{ eV},$$

$$V = 0.65 \text{ eV},$$

$$\Delta t = 0.47 \text{ eV},$$

$$t_h = 0,\qquad (18)$$

where U and V are on-site and nearest-neighbor Coulomb repulsions. The choice $t_h = 0$ is motivated by the fact that for low hole concentration the high-T_c oxides show activated behavior in the resistivity; we will show below also results for $t_h \neq 0$, which are qualitatively similar. We assume a flat density of states for simplicity, $g = 1/(8(t_h + n\Delta t))$. We have checked that results are very similar using the two-

dimensional tight-binding band structure in the low-density range of interest, as was also found in previous work [6]. We use a fixed chemical potential when varying the temperature. In the superconducting state, we find the number of particles to be essentially unchanged with temperature when the chemical potential is kept fixed. In the normal state a weak variation of density with temperature occurs when the chemical potential is kept fixed; however, such a variation is not unphysical and may in fact explain various observations in the normal state of high-T_c oxides [8,9].

Figure 2 shows the expectation values of the kinetic energy operators plotted versus temperature for various hole densities. Note the sharp change in the total kinetic energy when the system becomes superconducting. It can be seen that the single-particle part of the kinetic energy $\langle T_\delta^t \rangle$ indeed remains constant when entering the superconducting state. Thus we have simply from eq. (14)

$$\delta A_h = \frac{\pi e^2 a_\delta^2}{2\hbar^2} \langle -T_\delta^{\delta t} \rangle \, . \tag{19}$$

We also show δA_l given by eq. (15). Note that both low and high frequency missing areas approach zero linearly as T approaches T_c. For δA_h this is easily understood from eq. (17b), which is proportional to the square of the gap amplitude; for δA_l this is the well-known behavior of the London paramagnetic kernel. For calibration of the magnitude of these quantities, note that for free electrons with density n_e the full kinetic energy expectation value would be $\langle T_\delta \rangle /N = 0.52 n_e$ eV for lattice spacing $a = 2.7$ Å (the O–O planar distance in high-T_c oxides). Thus the oscillator strengths implied by fig. 2 are of order 1% of the total oscillator strength due to the electrons in this band.

It can be seen from fig. 2 that the high-frequency missing area becomes dominant for low hole concentration. In fig. 3 we show the behavior of the missing areas versus hole concentration, as well as T_c versus n. The same information is contained in the results reported for the various contributions to the London penetration depth in ref. [7]. For low hole concentration all the missing areas increase with n, since they are given by the product of the various pair mobilities [7] and the hole concentration. At higher n the high-frequency missing area decreases as the
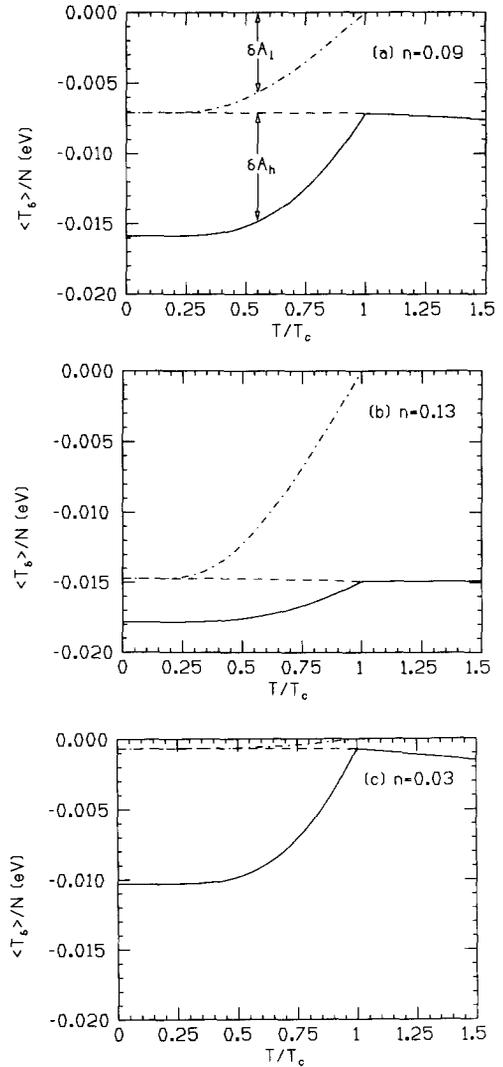

Fig. 2. Average kinetic energy per lattice site vs. temperature for various hole densities, for parameters in eq. (18). Full line: total kinetic energy $\langle T_\delta \rangle$ (eq. (13)); dashed line: single particle contribution $\langle T_\delta^t \rangle$, eq. (17a). Note that $\langle T_\delta^t \rangle$ is essentially temperature independent. The difference between the full and dashed lines gives the pair contribution eq. (17b), which is proportional to δA_h. The dash-dotted line is obtained by adding to the single particle contribution the paramagnetic kernel term (see eq. (15)), and it proportional to δA_l. The kinetic energy per site for nN carriers with free electron mass would be -0.047 eV, -0.068 eV and -0.016 eV for cases (a), (b) and (c) respectively.

coherence length monotonically increases [10] and the importance of pair hopping processes is reduced. For the parameters of eq. (18), at the maximum T_c,

δA_h dominates the total missing area and hence the London kernel. However, this will vary with other parameters in the model. In fig. 3(b) we show an example with $t_h \neq 0$ where the low- and high-fre-
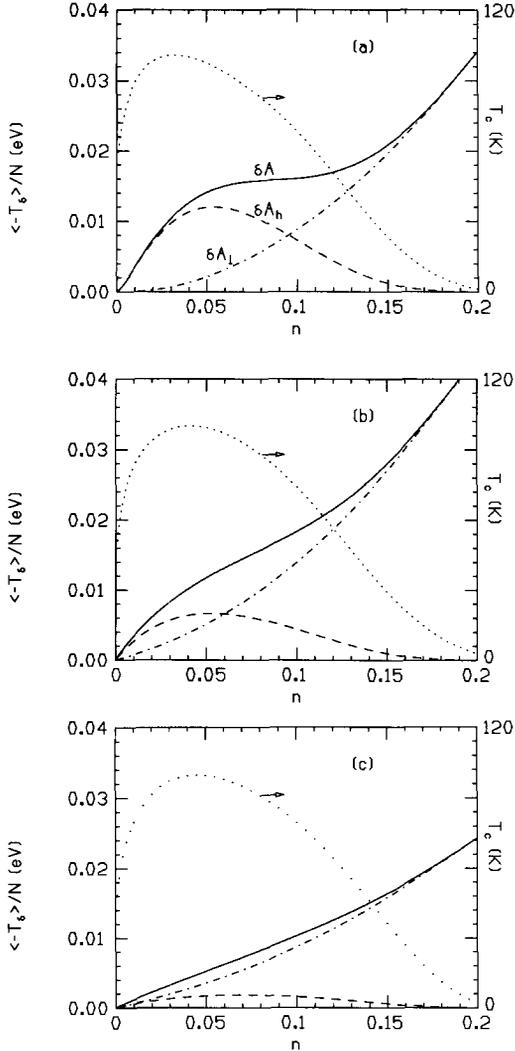

Fig. 3. Average kinetic energy per lattice site at zero temperature vs. hole concentration. Parameters are: (a) $U=5$ eV, $V=0.65$ eV, $\Delta t=0.47$ eV, $t_h=0$; (b) $U=5$ eV, $V=0.56$ eV, $\Delta t=0.45$ eV, $t_h=0.03$ eV; (c) $U=5$ eV, $V=0$, $\Delta t=0.19$ eV, $t_h=0.03$ eV. Full line is total kinetic energy, dashed and dash-dotted lines give single particle and pair contributions (eq. (17)). (Free electrons would yield a straight line with slope 0.52 for assumed lattice spacing.) As t_h increases or as V and Δt decrease, the relative contribution of the pair kinetic energy decreases. The behavior of T_c vs. hole concentration obtained from solution of the BCS equation is also shown (dotted lines, right scale).

quency missing areas give comparable contributions at the maximum T_c. Finally, fig. 3(c) shows an example where the low-frequency missing area dominates at all hole densities. However, we do not expect this parameter range, with $V=0$ and $t_h \neq 0$, to be realistic for the high-T_c oxides. Note also that the total missing area varies slower than proportional to n at intermediate values of n when $V \neq 0$, an effect discussed in ref. [7] that arises from the behavior of the pair mobility as a function of the single-particle hopping amplitude.

It is also interesting to consider the extreme strong coupling regime of this model, where holes are localized in the normal state and become mobile in the superconducting state [11], which will occur if $(t_h + n\Delta t)$ becomes zero for finite n. In that case there is no low-frequency missing area since there is no intra-band optical absorption in the normal state. There is, however, a finite London penetration depth determined by the pair mobility, and hence high-frequency missing area.

One may ask whether the features discussed here are unique to the model of hole superconductivity. For example, does one expect in the attractive Hubbard model [12] a change in the average kinetic energy with temperature? In the weak coupling regime $(|U| \ll t)$ no such change is expected, similarly as we found for $\langle T_\delta' \rangle$ in the model discussed here. In the strong coupling regime $(|U| \gg t)$ pre-formed pairs exist above T_c, with kinetic energy proportional to $t^2/|U|$; while the average kinetic energy will change at higher temperature when the pairs dissociate, one would not expect a change at low temperatures associated with the transition to the superconducting state. Thus in either regime no sharp changes in $\langle T_\delta \rangle$ should occur upon entering the superconducting state in this model, and hence no change in the high-frequency conductivity.

There have been other models proposed recently where the kinetic energy of carriers may change upon pairing [13,14] and thus one may expect consequences similar to the ones discussed here. We are not aware of explicit calculations for these models that address this question [15].

In summary, we have pointed out that in certain superconductors the usual relation between conductivity missing area in the frequency range of the superconducting energy gap and London penetration

depth or low-frequency imaginary conductivity will not hold. The difference between these quantities and their value expected from the low-frequency missing area is due to a change in the carrier kinetic energy and thus signals the existence of a kinetic pairing mechanism. Furthermore, this difference should show up at frequencies much larger than the superconducting energy gap, of order of the energy scale for optical transitions to other nearby bands, hence probably in the near infrared or visible range. The model of hole superconductivity provides an explicit realization of this scenario and yields predictions for the temperature and doping dependence of the various observables. Since the carriers become more mobile in the superconducting state the model predicts a reduced absorption (and consequently increased reflection) at high frequencies. At low frequencies, electromagnetic absorption in this model follows conventional BCS behavior (some differences occur at low hole concentration due to the narrowness of the band); explicit calculations are reported in ref. [16].

It is interesting to note that in the early days of superconductivity (pre-BCS) a change in high-frequency conductivity was in fact expected and systematically looked for [17–19], as it was thought that superconductors might be "particularly good reflectors of high-frequency radiation" [18]. No such change was reportedly found to within about 0.3% for "conventional" materials such as tin and lead. The considerations here suggest that it may be profitable to renew this search, particularly in materials with high transition temperature. For the high-T_c oxides, experimental evidence for a "high-frequency" missing area has recently been reported [20] in near-infrared absorption experiments on $YBa_2Cu_3O_{7-\delta}$.

Note added in proof: a more detailed recent analysis shows that the change in high-frequency conductivity can have considerably more structure than suggested by fig. 1 (to be published).

Acknowledgements

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