Theory of Raman scattering from gap excitations in weakly coupled high-temperature superconductors

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A theory of Raman scattering from gap excitations in high-temperature superconductors is presented in which a spin-density-wave gap g is treated on an equal footing with the superconducting gap Δ. Calculations are carried out in the weak-coupling regime, for which the Hubbard energy I is assumed to be much less than the bandwidth W. An electronic scattering cross section for $T=0$ is calculated which shows a definite threshold dependent on both g and Δ.

INTRODUCTION

One of the key problems in the newly discovered high-temperature superconductors is understanding the nature of the energy gap in these materials. Tunneling,[1] infrared absorption,[2] and Raman scattering[3–5] are some of the techniques used to characterize the gap structure. A simple BCS theory would give an energy gap which defines the threshold for scattering. However, two recent Raman experiments[3,4] are in disagreement with each other regarding the existence of such a gap. Cooper and Klein[3] observe the presence of residual electronic scattering well below the gap onset and this indicates that a continuum of electronic states exists inside the gap. Their conclusion is reinforced by interference of the interband electronic continuum scattering with phonons. Lyons *et al.*,[4] on the other hand, conclude that their data show an energy gap of 2Δ at about 25 meV.

On the theoretical side, several authors have addressed the problem of Raman scattering in superconductors.[6–8] Cuden[6] calculated the electronic Raman effect in superconductors for the case when the optical penetration depth δ is much less than the coherence length ξ_0, which corresponds to the large q limit (since $q \sim 1/\delta$). Dierker *et al.*,[7] on the other hand, derived an expression for the Raman amplitude using the BCS theory in the $q \rightarrow 0$ limit. Subsequently, Klein and Dierker[8] formulated a theory of Raman scattering in superconductors which extended the analysis to include gap anisotropy and finite q. Yet, all of these papers were before the high-T_c era and so do not include the physical effects peculiar to high-temperature superconductors.

In this paper we present a theory of Raman scattering from gap excitations in the high-temperature superconductors, incorporating the essential theoretical ingredients appropriate to these materials. Attention will be focused on the $q \rightarrow 0$ limit, a situation appropriate to small coherence length materials. The point is that here the superconductivity transition has an intimate relationship with the antiferromagnetic spin correlations observed in these materials over distances that are large compared to the lattice spacing. Schrieffer *et al.*[9] have proposed a high-temperature theory of superconductivity based on the spin-bag mechanism. The essential feature of this theory is that the pairing interaction occurs between Bloch states in the presence of spin-density waves (SDW). This intimate relationship between antiferromagnetism and superconductivity has been seen in the neutron-scattering experiments of Shirane *et al.*[10] and Vaknin *et al.*[11] It is therefore natural to include not only the superconducting gap Δ but also the SDW gap g on an equal footing in any theory of Raman scattering in the high-T_c materials. When this is done, it is found that the Raman line shape depends strongly on the ratio of g to Δ. Two kinds of excitations, quasiparticle and pair, are possible and both contribute to the Raman amplitude. From this it emerges that the threshold for scattering is given both by g and Δ, which are determined self-consistently. The cross section rises sharply above this threshold and then falls away gradually on the high-energy side of the maximum. The solutions do not allow gap states, so we do not predict continuum scattering below the threshold. The combination of the SDW and superconducting pair aspects of the theory should allow us to give a quantitative interpretation of Raman scattering experiments in weakly coupled high-temperature superconductors.

HAMILTONIAN AND GAP EQUATIONS

We introduce a single-band Hubbard Hamiltonian

$$H=\sum_{\substack{i,j\\ \sigma}} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + I \sum_{i} n_{i\uparrow} n_{i\downarrow} , \tag{1}$$

where the first term is the kinetic energy of the electrons and the second term is the on-site Coulomb repulsion of strength I between electrons in the usual way. Linearizing, we get

$$H=\sum_{\substack{i,j\\ \sigma}}T_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+I\sum_{i,\sigma}(\langle c_{i\sigma}^{\dagger}c_{i\sigma}\rangle c_{i,-\sigma}^{\dagger}c_{i,-\sigma}-\tfrac{1}{2}\langle c_{i\sigma}^{\dagger}c_{i,-\sigma}^{\dagger}\rangle c_{i\sigma}c_{i,-\sigma}-\tfrac{1}{2}\langle c_{i\sigma}c_{i,-\sigma}\rangle c_{i\sigma}^{\dagger}c_{i,-\sigma}^{\dagger}) . \tag{2}$$

This linearization allows us to define, after Fourier transformation, two order parameters,

$$g^{\sigma}=I\sum_{k}\langle c_{k+Q,\sigma}^{\dagger}c_{k\sigma}\rangle \tag{3}$$

and

$$\Delta=-I\sum_{k}\langle c_{k\uparrow}c_{-k\downarrow}\rangle , \tag{4}$$

which we identify as the SDW gap and the superconducting gap, respectively (restricting our analysis to a single value of Q). It should be emphasized that the linearization carried out above is valid when $I<W$, where W is the bandwidth. This automatically implies that $g,\Delta<W$.

The 4×4 Hamiltonian matrix[12] of Eq. (2) may be represented in the four states

$$c_{k\uparrow}|0\rangle,\ c_{-k\downarrow}^{\dagger}|0\rangle,\ c_{k+Q,\uparrow}|0\rangle \text{, and } c_{-k+Q,\downarrow}^{\dagger}|0\rangle ,$$

where $|0\rangle$ is to be interpreted either as the hole or electron vacuum as appropriate; explicitly in this basis it is

$$H=\begin{bmatrix}\varepsilon_k & g & \Delta & 0\\ g & \varepsilon_{K+Q} & 0 & \Delta\\ \Delta & 0 & -\varepsilon_k & -g\\ 0 & \Delta & -g & -\varepsilon_{K+Q}\end{bmatrix} . \tag{5}$$

Within (5) we have assumed that

$$\Delta_Q=-I\sum_{k}\langle c_{k+Q\uparrow}c_{-k+Q\downarrow}\rangle=\Delta .$$

The energy eigenvalues and eigenvectors of Eq. (5) are obtained through a generalized Bogoliubov-Valatin transformation (given in the Appendix). The energies are

$$E_{kn}=\pm\frac{1}{\sqrt{2}}\{2\Delta^2+2g^2+\varepsilon_k^2+\varepsilon_{k+Q}^2\pm(\varepsilon_k+\varepsilon_{k+Q})\times[4g^2+(\varepsilon_k-\varepsilon_{k+Q})^2]^{1/2}\}^{1/2} , \tag{6}$$

where the choice of signs for the different eigenvalues follows the convention $(-,+)$, $(+,+)$, $(-,-)$, and $(+,-)$ for $n=1$, 2, 3, and 4, respectively. Apart from the half-filled band case, when $\varepsilon_k=-\varepsilon_{k+Q}$, this leads to four distinct states whose energy levels are split by amounts depending on Δ and g. Solution of the equations for Δ and g yield a phase diagram in which antiferromagnetism and superconductivity coexist.[12–14] Using the eigenvectors of Eq. (5) (the specific forms appear in the Appendix), we can write the two gap equations as

$$\Delta=I\sum_{k,n}(\Gamma_{n,2}\Gamma_{n,4}+\Gamma_{n,3}\Gamma_{n,1})f_{kn} , \tag{7}$$

$$g=2I\sum_{k,n}[\Gamma_{n,2}\Gamma_{n,1}f_{kn}+\Gamma_{n,3}\Gamma_{n,4}(1-f_{kn})] . \tag{8}$$

The Γ_{nm} are elements of a generalized Bogoliubov-Valatin transformation matrix given in the Appendix; the f_{kn} are the Fermi distribution functions for the eigenstates associated with the energies E_{kn},

$$f_{kn}=\frac{N}{\exp(\beta E_{kn})+1} ,$$

where N is a normalization factor. Using these terms, the band filling may be expressed as

$$N_e=\frac{1}{2}\sum_{k}\sum_{n}[(\Gamma_{1n}^2+\Gamma_{2n}^2)f_{kn}+(\Gamma_{3n}^2+\Gamma_{4n}^2)(1-f_{kn})] . \tag{9}$$

As expressed, N_e has a maximum value of 2. The new eigenstates of the system, associated with the energies of Eq. (6), define states in terms of pair and quasiparticle excitations, and the Raman spectrum is thus given in relation to these excitations.

Equations (7)–(9) are solved self-consistently, assuming a tight-binding band structure of the form

$$\varepsilon_k=-\tfrac{1}{4}W[\cos(k_xa)+\cos(k_ya)]+\text{const} ,$$

where W is the bandwidth. It is convenient to define two related energy parameters, namely

$$x_k=-\tfrac{1}{2}(\varepsilon_k-\varepsilon_{k+Q})+\text{const}$$
$$=-\tfrac{1}{4}W[\cos(k_xa)+\cos(k_ya)]+\text{const}$$

and

$$y_k=\tfrac{1}{2}(\varepsilon_k+\varepsilon_{k+Q})+\text{const}=\text{const} .$$

Setting a value for the second parameter y_k is equivalent to fixing the position of the Fermi surface.[11]

To simultaneously solve Eqs. (7) and (8), we first divide through by Δ and g, respectively; then, with Δ and g fixed, we equate the right-hand sides of the equations since the left-hand side of each is equal to unity. A numerical routine varies y until this new equation is satisfied. Having fixed g, Δ, and y, we can substitute back into either (7) or (8) for I. The electronic band filling follows from (9).

The numerical solution of the above-mentioned set of equations for $T=0$ is given in Fig. 1, where the self-consistent solutions for Δ and g are graphed as a family of contours over the I-N_e plane. All energies in the figure are measured in terms of the bandwidth W. In finding these solutions, assuming a to be the lattice spacing, we have taken $\mathbf{Q}=\pi(\hat{\mathbf{x}}+\hat{\mathbf{y}})/a$, that is near half-filling. Because we are interested only in the weak-coupling regime $I<W$ only solutions for which $I/W<0.3$ have been considered.

As can be seen from Fig. 1, superconductivity and spin-density waves coexist in the given range of values of I and N_e, however, the functional dependencies of Δ and g with N_e are quite different. Arbitrarily close to the half-filled band case ($N_e=1$), only solutions for which Δ tends to zero asymptotically appear to be valid. There is no similar restriction of g, which approaches a constant value monotonically. Thus as $N_e\to1$, $\Delta\to0$ and $g\propto I$, implying that the system is purely antiferromagnetic at half-filling. Moving away from half-filling, our solutions show an increasing preference for the superconducting solution at the expense of the SDW one. We note that both g and Δ approach zero as $I\to0$, as we would expect. These re-

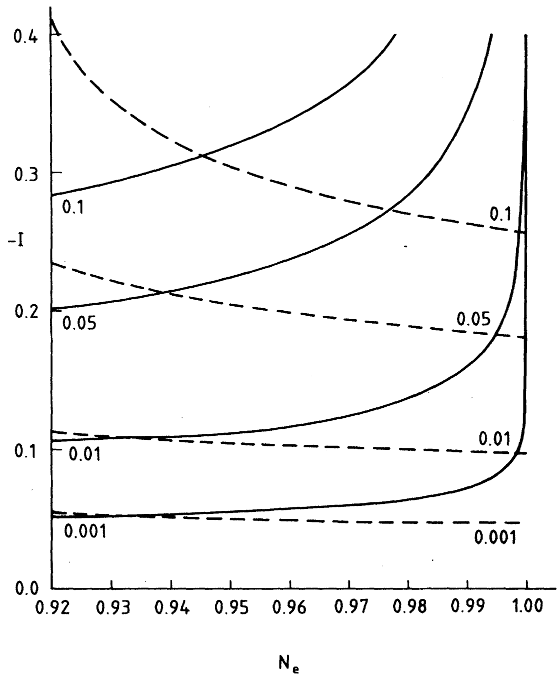

FIG. 1. Self-consistent solutions of the gap equations: Contours of constant Δ (——) and constant g (---) as functions of the Hubbard I and the electron band filling N_e. The numbers to the right label the g contours, those to the left label the Δ contours.

sults are consistent with those of Inue *et al.*,[13] who dealt with the problem in the strong coupling limit. They found that for $W/I \sim 0.3$, superconductivity and antiferromagnetism coexist for $N_e \sim 0.7$; for lower values of N_e the system became purely superconducting.

ELECTRONIC RAMAN SCATTERING CROSS SECTION

The differential scattering cross section is usually written as

$$\frac{d^2\sigma}{d\Omega\, d\omega} = r_0^2 \frac{\omega_2}{\omega_1} \sum_{i,f} |\langle f | \chi_{\mu\nu} | i \rangle|^2 (P_i - P_f) \times \delta[\omega - (E_f - E_i)] , \qquad (10)$$

where P_i and P_f are the thermal factors which describe the occupation probability of the initial and final states, $\omega = \omega_1 - \omega_2$ is the energy transfer, and $\chi_{\mu\nu}$ is the transition susceptibility tensor. For the present, we restrict ourselves to electronic transitions appropriate to gap excitations and neglect phonon excitations.

There are two contributions to the susceptibility tensor: One coming from the $\mathbf{A}\cdot\mathbf{A}$ term corresponding to intraband scattering and the other from the $\mathbf{A}\cdot\mathbf{P}$ term which gives interband scattering. ($\mathbf{A}$ is the vector potential of the photon field.) We confine ourselves to the latter term which gives the leading contribution for the case we are considering.

A straightforward calculation yields

$$\frac{d^2\sigma}{d\Omega\, d\omega} = r_0^2 \frac{\omega_2}{\omega_1} \mathrm{Im} \left[\sum_k \sum_{m \neq n} \frac{f_{k,n} - f_{k+q,m}}{E_{k+q,m} - E_{k,n} - \hbar\omega} |c_k^s(q)|^2 |A_k^{nm}(\omega_1)|^2 + \sum_k \sum_{m,n} (1 - f_{k,n} - f_{k+q,m}) |c_k^a(q)|^2 |B_k^{mg}(\omega_1)|^2 \times \left(\frac{1}{E_{k+q,m} + E_{k,n} + \hbar\omega} + \frac{1}{E_{k+q,m} + E_{k,n} - \hbar\omega} \right) \right] , \qquad (11)$$

where the first term corresponds to quasiparticle excitations and the second to pair excitations.

Here $A_k(\omega_1)$ and $B_k(\omega_1)$ are the Raman tensors given by

$$A_k^{nm}(\omega_1) = \sum_i \left[\frac{\langle m | \mathbf{p}\cdot\boldsymbol{\varepsilon}_2 | i \rangle \langle i | \mathbf{p}\cdot\boldsymbol{\varepsilon}_1 | n \rangle}{E_{kn} - E_{ki} + \hbar\omega_1} + \frac{\langle m | \mathbf{p}\cdot\boldsymbol{\varepsilon}_1 | i \rangle \langle i | \mathbf{p}\cdot\boldsymbol{\varepsilon}_2 | n \rangle}{E_{kn} - E_{ki} - \hbar\omega_2} \right] \qquad (12)$$

and

$$B_k^{mg}(\omega_1) = \sum_i \left[\frac{\langle m | \mathbf{p}\cdot\boldsymbol{\varepsilon}_2 | i \rangle \langle i | \mathbf{p}\cdot\boldsymbol{\varepsilon}_1 | g \rangle}{E_{kg} - E_{ki} - \hbar\omega_1} + \frac{\langle m | \mathbf{p}\cdot\boldsymbol{\varepsilon}_1 | i \rangle \langle i | \mathbf{p}\cdot\boldsymbol{\varepsilon}_2 | g \rangle}{E_{kg} - E_{ki} + \hbar\omega_2} \right] \qquad (13)$$

and together they determine the resonance behavior of the Raman cross section. Here, E_{ki} are the energies of the higher bands and E_{kg} is the ground-state energy. The Raman tensors will be slowly varying functions of k in an off-resonance situation and this is what we will assume. The functions $c_k^s(q)$ and $c_k^a(q)$ in Eq. (11) are the coherence factors resulting from the generalized Bogoliubov-Valatin transformation.

The above expressions hold for arbitrary values of q, but in the limit $q \to 0$, Eq. (11) reduces to

$$\frac{d^2\sigma}{d\Omega\, d\omega} = r_0^2 \frac{\omega_2}{\omega_1} \mathrm{Im} \left[\lim_{\eta \to 0} \sum_k \sum_{m \neq n} \frac{f_{k,n} - f_{k,m}}{E_{km} - E_{kn} - \hbar\omega + i\eta} |A_k^{nm}(\omega_1)|^2 \right] , \qquad (14)$$

since $c_k^s(0) = 1$ and $c_k^a(0) = 0$. A continuum of excitations corresponding to the energy difference $E_{km} - E_{kn}$ contributes to the cross section.

The Raman cross section was calculated numerically from Eqs. (6) and (14) for various values of the parameters g and Δ; a typical result at $T=0$ is illustrated in Fig. 2. For this case, the values $g/W=\Delta/W=0.0025$ were chosen, with the bandwidth W set to 5 eV. For these values, $2\Delta=200\ \text{cm}^{-1}$. (This should not be confused with the observed gap since that is also a function of g.) We note that the spectrum shows a definite threshold for Raman scattering with a slower and more gradual drop on the high-energy side of the maximum. A similar behavior was observed for a wide range of g and Δ values. Raising the temperature shifts the electronic spectral weight towards higher energies and broadens the spectrum, but the form of the spectrum remains exactly the same as at $T=0$ (the range $T<100$ K was tested).

It is appropriate to compare our theoretical results with the available data.[3,4] Lyons *et al.*[4] have found an energy gap of about 200 cm^{-1} but conclude that the Raman response should be smeared due to the anisotropy of the material. They do not, however, provide a quantitative fit to their data. The spectra of Ref. 3 do not show any structure appropriate to an energy gap. Instead, the shape of the spectrum is reminiscent of electronic Raman scattering in semiconductors,[15] where there is relatively weak energy dependence. Residual scattering, if any, within the gap should exhibit a much faster decline below the gap. In terms of our model, very low-frequency excitations would be possible only when both Δ and g approach zero, which seems unphysical for the high-T_c superconductors. The cause of the low-frequency excitations seen in Ref. 3 remains unclear, and we can give no clear theoretical explanation for them. Gap suppression due to Gaussian fluctuations in the order parameter over a sizable temperature range near a boundary has been discussed in $YBa_2Cu_3O_7$ by Deutscher and Müller,[16] where the correlation length ξ_0 is very small. This effect is enhanced when the boundary is perpendicular to the c axis, so that the gapless tunneling could be interpreted in terms of the strongly diminished gap. Perhaps the states seen by Cooper and Klein[3] are a manifestation of such a gap suppression. Convoluting the calculated Raman response into a function to include gap anisotropy would smear the edge and also produce low-energy states. But the incoherent nature of this procedure would obscure the antiresonant effects alluded to in the Introduction. Probably the observed gap states result from a combination of gap anisotropy and gap suppression due to the short coherence length.

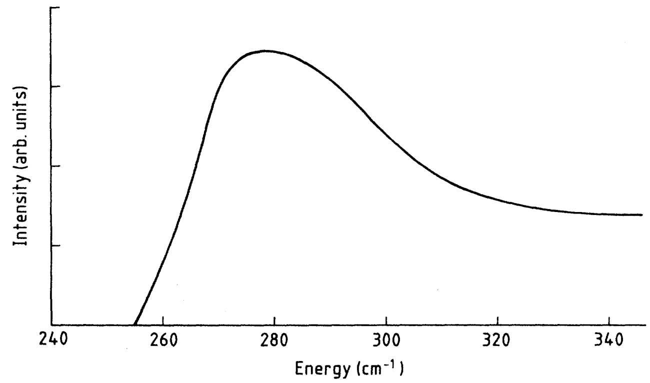

FIG. 2. The Raman cross section at $T=0$ for $g=\Delta=100\ \text{cm}^{-1}$, with $W=5$ eV.

We conclude by noting that in the theory presented here, we have neglected the collective modes due to amplitude fluctuations in the SDW ground state. Inclusion of these would probably lead to a bound state within the gap similar to the mode due to coupling between a charge-density-wave amplitude mode and the superconducting order parameter.[17]

APPENDIX

We define the Γ matrix as that unitary matrix which acts as a generalized Bogoliubov-Valatin transformation in the space of Eq. (5). We begin by defining its inverse, $[\Gamma]^{-1}$:

$$\begin{bmatrix} \gamma_k^1 \\ \gamma_k^2 \\ \gamma_k^3 \\ \gamma_k^4 \end{bmatrix} = \begin{bmatrix} \frac{1}{N_1} & \frac{-2x+D}{2gN_1} & \frac{2\Delta}{N_1(2E_{k1}+2y-D)} & \frac{(-2x+D)(E_{k1}+x-y)-2g^2}{2N_1 g\Delta} \\ \frac{1}{N_2} & \frac{-2x+D}{2gN_2} & \frac{2\Delta}{N_2(2E_{k2}+2y+D)} & \frac{(-2x+D)(E_{k2}+x-y)-2g^2}{2N_2 g\Delta} \\ \frac{1}{N_3} & \frac{-2x-D}{2gN_3} & \frac{2\Delta}{N_3(2E_{k3}+2y-D)} & \frac{(-2x+D)(E_{k3}+x-y)2g^2}{2N_3 g\Delta} \\ \frac{1}{N_3} & \frac{-2x-D}{2gN_4} & \frac{2\Delta}{N_4(2E_{k4}+2y+D)} & \frac{(-2x+D)(E_{k4}+x-y)-2g^2}{2N_4 g\Delta} \end{bmatrix} \begin{bmatrix} c_{k\uparrow} \\ c_{k+Q\uparrow} \\ c^\dagger_{-k\downarrow} \\ c^\dagger_{-k+Q\downarrow} \end{bmatrix},$$

where $|\gamma^i\rangle$ is the ith eigenvector of Eq. (5). $[\Gamma]$ is obtained by transposition since the matrix is unitary. Thus $[\Gamma_{ij}]^{-1}=[\Gamma_{ji}]$. The N_i in the above matrix are normalization factors defined as

$$N_i^2=1+\frac{[x-\frac{1}{2}\alpha(i)D]^2}{g^2}+\frac{\Delta^2}{[E_{ki}^2+y+\frac{1}{2}(-1)^j D]^2}+\frac{\{[x-\frac{1}{2}\alpha(i)D](E_{ki}^2+x-y)+g^2\}^2}{g^2\Delta^2},$$

in which $\alpha(1)=\alpha(2)=-\alpha(3)=-\alpha(4)=1$.

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