Surface contribution to Raman scattering from layered superconductors

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Generalizing recent work, the Raman-scattering intensity from a semi-infinite superconducting superlattice is calculated taking into account the surface contribution to the density response functions. Our work makes use of the formalism of Jain and Allen developed for normal superlattices. The surface contributions are shown to strongly modify the bulk contribution to the Raman-spectrum line shape below 2Δ, and also may give rise to additional surface plasmon modes above 2Δ. The interplay between the bulk and surface contribution is strongly dependent on the momentum transfer $q_\parallel$ parallel to layers. However, we argue that the scattering cross section for the out-of-phase phase modes (which arise from interlayer Cooper pair tunneling) will not be affected and thus should be the only structure exhibited in the Raman spectrum below 2Δ for relatively large $q_\parallel \sim 0.1\Delta/v_F$. The intensity is small but perhaps observable. [S0163-1829(96)01433-6]

I. INTRODUCTION

Recently, the authors[1] studied the inelastic light-scattering intensity of an infinite superconducting superlattice with a bilayer basis. Motivated by the Cooper pair tunneling model proposed by Chakravarty and co-workers[2] for high-T_c layered superconductors, we discussed the in-phase and out-of-phase phase modes (corresponding to the phase fluctuations of the two superconducting order parameters in a bilayer) which arise in the presence of interlayer Cooper pair tunneling.[3] These modes couple into density fluctuations and, as a result, show up in the Raman inelastic light scattering. The intensity is weak because of screening associated with the Coulomb interaction, and in fact is below the threshold of current Raman experiments. However, our results are of sufficient interest that such experiments should be attempted. In this paper, we extend our previous calculations[1] and show how the Raman spectrum for $\omega < 2\Delta$ is significantly modified when we include the surface contribution. We also include surface plasmons (which occur above 2Δ) in the calculation of the Raman intensity of layered superconductors.

The present paper is based on the approach of Jain and Allen,[4] who considered normal layered electron gas (LEG). In their calculation for a semi-infinite superlattice, both the bulk and surface contributions were included. They found that there were two effects of the surface: (1) Van Hove singularities at the upper and lower limits of the bulk plasmon band were completely canceled out by negative surface contributions. (2) Depending on the background dielectric constants, surface plasmons[5] can appear, either above or below the bulk plasmon band. We show that the analogous effects arise in a semi-infinite *superconducting* superlattice, resulting in major modifications of the bulk contribution to the Raman-scattering spectrum given in Ref. 1. Apart from the out-of-phase phase mode contribution, the Raman-scattering intensity is found to be strongly dependent on the value of momentum transfer $q_\parallel$ (parallel to the layers). For simplicity, we only discuss the surface effects for a superlattice with a single layer per unit cell. This is sufficient to understand the essential physics.

The isotropic inelastic light-scattering cross section is given by[4,6]

$$\frac{d\sigma}{d\omega d\Omega} \propto |\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_f|^2 I(\mathbf{q},\omega), \tag{1}$$

where

$$I(\mathbf{q},\omega) = \sum_{\substack{l,l' \\ i,j}} \mathrm{Im}\chi_{ij}(\mathbf{q}_\parallel,\omega,l,l') e^{-(Z_{l,i}+Z_{l',j})/\delta} e^{-2ik_\perp(Z_{l,i}-Z_{l',j})}. \tag{2}$$

Here $Z_{l,i}$ represents the position of the ith layer in the lth unit cell. The density response function $\chi_{ij}(\mathbf{q}_\parallel,\omega,l,l')$ in Eq. (2) has been evaluated in Ref. 1 and represents the correlation between the charge density on layer (l,i) and the charge density on layer (l',j). The incident photon has momentum $\mathbf{k}_i$, energy ω_i, and polarization $\hat{\mathbf{e}}_i$ and the scattered photon is similarly described by $\mathbf{k}_f$, ω_f, and $\hat{\mathbf{e}}_f$. We assume that the energy transfer $\omega \equiv \omega_i - \omega_f$ in Eq. (2) is very small compared to the photon frequencies, i.e., $\omega_i \simeq \omega_f$. The momentum transfer parallel to the interface is $\mathbf{k}_{\parallel,i} - \mathbf{k}_{\parallel,f} \equiv \mathbf{q}_\parallel$ and the momentum perpendicular to the interface is $k_{z,i} - k_{z,f} \equiv q_z$. For small-angle scattering, we have $\mathrm{Re}q_z \simeq 2k_\perp$ and $\mathrm{Im}q_z \simeq \delta^{-1}$ where $k_\perp$ is the momentum carried by the incident photon and δ describes the damping of the photons in the medium. The result given in Eq. (2) shows that as a result of the finite value of δ, the inelastic light-scattering cross section involves a *weighted* sum of the correlation functions for electronic densities in the different layers. We are interested in the interplay between the bulk and surface contributions to the Raman spectra. For this purpose, we only keep the *isotropic* matrix element for the Raman interaction given in Eq. (1).[7] We consider superconductors with an s-wave layer pairing interaction but similar calculations could be done for d-wave superconductors, as discussed in Refs. 3 and 8.

II. BULK IN-PHASE AND OUT-OF-PHASE PHASE MODES

For later comparison, we first recall the results of Ref. 1 for the Raman spectra for an infinite superconducting *bilayer* superlattice, ignoring the surface contributions. One finds that Eq. (2) reduces to

$$I(\omega)=\frac{1}{1-e^{-2c/\delta}}\,\mathrm{Im}\Bigg\{\frac{E_+}{2}(1+e^{-2d/\delta}+2e^{-d/\delta}\cos 2k_\perp d)\times\left[1+\frac{2v_{2\mathrm{D}}E_+\sinh q_\| c(u^2e^{2c/\delta}-1)}{F\sqrt{b^2-1}}\right]+\frac{E_-}{2D_-}(1+e^{-2d/\delta}-2e^{-d/\delta}\cos 2k_\perp d)\Bigg\}, \qquad (3)$$

where we have introduced the functions

$$b\equiv\cosh q_\| c-2v_{2\mathrm{D}}E_+\sinh q_\| c,$$

$$u\equiv b+\sqrt{b^2-1},$$

$$F\equiv u^2e^{2c/\delta}-2ue^{c/\delta}\cos 2k_\perp c+1,$$

$$D_-=1-v_{2\mathrm{D}}(1-e^{-q_\| d})E_- . \qquad (4)$$

The spacing of the bilayer is d, the unit cell length is c, $v_{2\mathrm{D}}\equiv 2\pi e^2/q_\|\epsilon$ is the two-dimensional (2D) Coulomb interaction, and ϵ is the superlattice background static dielectric constant. In the long-wavelength limit ($q_\|\ll 2\Delta/v_F$), the functions $E_\pm(\mathbf{q}_\|,\omega)$ are given by[3,1]

$$E_\pm=\frac{1}{4}N(\epsilon_F)J(\overline{\omega})\left[\frac{-R_\pm+\frac{1}{8}\overline{q_\|^2}J(\overline{\omega})}{R_\pm+\frac{1}{4}(\overline{\omega}^2-\frac{1}{2}\overline{q_\|^2})J(\overline{\omega})}\right], \qquad (5)$$

where we have defined

$$J(\overline{\omega})=\begin{cases}\dfrac{2}{\overline{\omega}\sqrt{1-\overline{\omega}^2}}\arcsin\overline{\omega}, & \overline{\omega}<1,\\[2ex] \dfrac{2}{\overline{\omega}\sqrt{\overline{\omega}^2-1}}\left[\ln(\overline{\omega}-\sqrt{\overline{\omega}^2-1})+i\dfrac{\pi}{2}\right], & \overline{\omega}>1,\end{cases} \qquad (6)$$

and

$$R_+=0,\quad R_-=\frac{1}{gN(\epsilon_F)}\frac{2x}{x^2-1},\quad x\equiv\frac{T_J}{g}. \qquad (7)$$

Here $\overline{\omega}\equiv\omega/2\Delta$, $\overline{q_\|}\equiv q_\| v_F/2\Delta$, $N(\epsilon_F)\equiv m^*/\pi$ is the 2D electronic density of states at the Fermi level with m^* being the effective electronic mass, g is the in-layer pairing interaction, and T_J is the interlayer Cooper pair tunneling strength. Replacing $\omega\to\omega+i\gamma$ is a simple way of including finite-energy resolution. On the right-hand side (rhs) of Eq. (3), the first term ($\equiv I_I$) gives the contribution from the in-phase phase fluctuations, while the second term ($\equiv I_O$) is associated with the out-of-phase phase fluctuations.

One finds that the in-phase first term in Eq. (3) has *three* poles, given by

$$F(2k_\perp,q_\|,\omega)=0 \quad \text{and} \quad b(q_\|,\omega)=\pm 1. \qquad (8)$$

$F=0$ gives an in-phase plasmon mode which Raman scattering picks up (in an approximate way,[4] this mode is similar to the plasmon mode of an infinite superlattice, with $q_z=2k_\perp$). The additional two (Van Hove) singularities given by the solutions of $b=\pm 1$ correspond to the upper (+) and lower (−) limits of the ''bulk plasmon'' band for an *infinite* superlattice.[4] In contrast, the second term in Eq. (3) only has a single pole given by

$$D_-(q_\|,\omega)=0, \qquad (9)$$

corresponding to out-of-phase phase mode discussed in detail in Ref. 1. Because the unit cell summation is over many bilayers, the Raman intensity is strongly enhanced in the superlattice case compared to the isolated bilayer case (the latter is discussed in Ref. 8). This is the origin of the prefactor $[1-\exp(-2c/\delta)]^{-1}\approx\delta/2c$ in Eq. (3). Using $c\equiv 12$ Å and $\delta\equiv 1000$ Å, this prefactor is ~40.

We note in Eq. (5) that, in the limit of $q_\|\to 0$, we have $R_+=0$ and hence $E_+\sim\overline{q_\|^2}\to 0$. This implies that the in-phase phase modes given by $F=0$ and $b=\pm 1$ have less weight when $q_\|$ is small, an expected consequence of the screening due to the Coulomb interaction. In contrast, even in the low-$q_\|$ limit, $E_-\sim R_-\sim x$ is still finite, being proportional to the pair tunneling strength T_J. This means that the out-of-phase phase mode given by $D_-=0$ has a weight proportional to x and is not too dependent on the value of $q_\|$ (in the range probed in Raman-scattering experiments). In addition, one can see from Eq. (3) that the intensities of I_I and I_O are also dependent on the factors $(1+e^{-2d/\delta}\pm 2e^{-d/\delta}\cos 2k_\perp d)$ which arise from the lattice summation in Eq. (2). Since $d\ll\delta$ and $k_\perp d\ll 1$, we see that the intensity for the out-of-phase phase modes (− sign) is greatly reduced compared to that of the in-phase phase modes (+ sign) as a result of these factors.

In Fig. 1, we plot the Raman light-scattering intensity based on Eq. (3). In this and other figures, we use the parameters: bilayer spacing $d=3$ Å, the unit cell size $c=12$ Å, pairing strength $gN(\epsilon_F)\equiv 0.25$, Fermi momentum $k_F=3.07\times 10^7$ cm^{-1} and hence a 2D hole density $n=1.5\times 10^{14}$cm^{-2}, layer effective mass $m^*=m$, background static dielectric constant $\epsilon=10$, photon momentum in the z direction $k_\perp=1.0\times 10^5$ cm^{-1}, optical penetration depth $\delta\sim 1/k_\perp=1000$ Å, superconducting energy gap $\Delta=280$ cm^{-1}, and finite-energy resolution $\gamma=0.05\Delta$. The momentum transfer parallel to the layers is

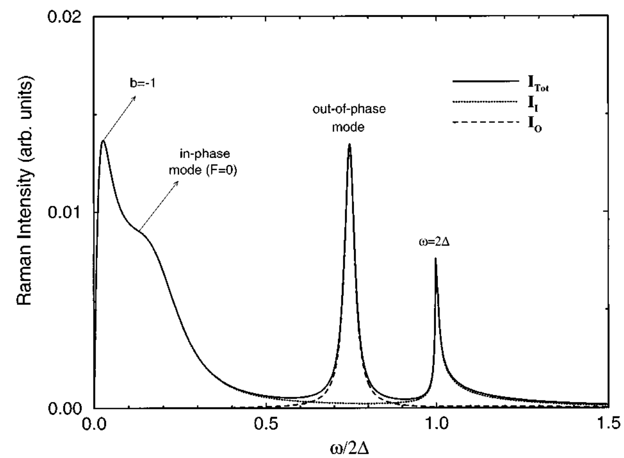

FIG. 1. The bulk Raman intensity (Ref. 11) given by Eq. (3) for an infinite superconducting bilayer superlattice with interlayer Cooper pair tunneling of amplitude T_J. We use $T_J=0.03g$ ($x=0.03$) and $q_\|=5.0\times 10^{-3}\Delta/v_F$. The surface contribution is not included.

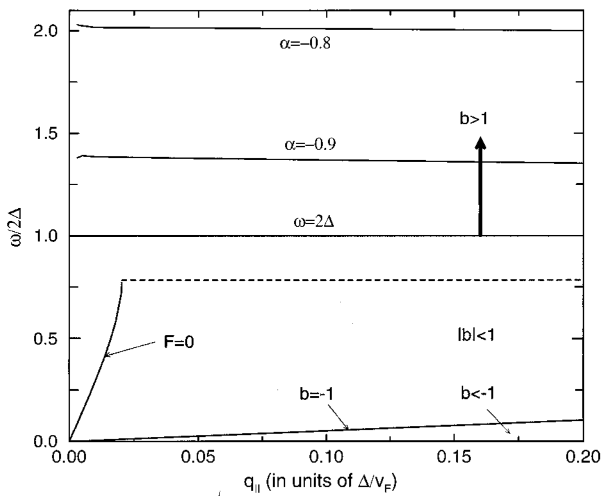

FIG. 2. The dispersion relation of surface plasmons in a semi-infinite superconducting superlattice (solutions of $Q=0$) for $\alpha=-0.8$ and -0.9. The shaded area between $b=-1$ and $\omega=2\Delta$ lines denotes the bulk plasmon band for an infinite superconducting superlattice. The $F=0$ line represents a sharp ''bulk plasmon'' picked up by Raman scattering. For $q_\parallel \gtrsim 0.025\Delta/v_F$ (dashed line), there is only an overdamped resonance (see Fig. 5).

$q_\parallel=5.0\times10^{-3}\Delta/v_F=1.17\times10^3\ \mathrm{cm}^{-1}$ in Fig. 1. The out-of-phase phase mode is well defined, as expected. While the Raman intensity from the out-of-phase contribution shown in Fig. 1 is not too dependent on the value of $q_\parallel$, roughly speaking, the intensity from the in-phase contribution is proportional to $q_\parallel^2$. As shown in Fig. 1 for the in-phase contributions, one has a small peak at $\omega=2\Delta$ corresponding to the pair-breaking gap in an *s*-wave superconductor (which is identical to the upper limit of the bulk plasmon band, i.e., the pole given by $b=1$). In addition, ''hidden'' in the low-frequency broadened peak is the in-phase phase mode contribution given by the solution of $F=0$, which overlaps on the Van Hove singularity corresponding to the pole $b=-1$ at the lower limit of the bulk superlattice plasmon band (see Fig. 2). This will become more transparent when we discuss the surface contribution.

In a normal metal superlattice,[4] the lower limit of the bulk plasmon band is far away from the particle-hole continuum and, as a result, both the upper ($b=+1$ pole) and lower ($b=-1$ pole) limits of the bulk plasmon band are well defined. We recall that the bulk plasmon band refers to the plasmons labeled by q_z in an *infinite* superconducting superlattice. These give rise to the Van Hove singularities discussed in Ref. 4. In contrast, in a superconducting superlattice, the particle-hole excitation spectrum (which begins at the pair-breaking gap 2Δ) is strongly coupled into the superlattice bulk plasmon spectrum. As a consequence, the bulk plasmon band is split into two different regions above and below the pair-breaking gap (2Δ). For the plasmon band below 2Δ (which we are most interested in), one can find a well-defined line for $b=-1$ corresponding to the lower band limit of the bulk plasmon band (which is generally at low frequencies). However, due to the strong coupling between the bulk plasmon and BCS particle-hole continuum, starting at 2Δ, there is no well-defined solution for $b=+1$. Nevertheless, the peak at 2Δ in Fig. 1 supports the argument that $\omega=2\Delta$ can be considered as the effective upper limit of a superconducting bulk plasmon band.[9,10]

As Jain and Allen[4] have pointed out for a normal superlattice with one layer per unit cell, the Van Hove singularity associated with $b=+1$ corresponds to all the neighboring layers oscillating in phase; while the one associated with $b=-1$ corresponds to all the neighboring layers oscillating out of phase with each other. In contrast, the out-of-phase phase mode in Fig. 1 is a collective mode associated with the ''internal Cooper pair dynamics'' exhibited by a bilayer via the interlayer Cooper pair tunneling between the two layers. The physics of this out-of-phase phase mode is completely different from the out-of-phase $b=-1$ bulk plasmon in a superlattice.

III. SURFACE CONTRIBUTIONS AND SURFACE PLASMONS

The result in Eq. (3) does *not* include the surface contribution. We now include it but only consider the case of a semi-infinite superlattice of a *single* layer per unit cell since this already describes the interplay between bulk and surface contributions. In the case of a single layer per unit cell, we need only to replace the usual 2D Lindhard function in the formulas given by Jain and Allen[4] by the appropriate density response function [i.e., E_+ in Eq. (5)] for a *neutral* 2D superconductor.[3] Using Eq. (50) in Ref. 4, we find that the resulting Raman intensity is given by

$$I(\omega)=\frac{1}{1-e^{-2c/\delta}} \times \mathrm{Im}\left\{ E_+\left[\left(1+\frac{v_{2D}E_+\sinh q_\parallel c(u^2e^{2c/\delta}-1)}{F\sqrt{b^2-1}}\right) + \frac{v_{2D}E_+(e^{2c/\delta}-1)(u^2A-2uB+C)}{2Q(b^2-1)F}\right]\right\}, \tag{10}$$

where we have defined

$$A\equiv G\sinh^2 q_\parallel c+1+\frac{\alpha}{2}e^{2q_\parallel c},$$

$$B\equiv H\sinh^2 q_\parallel c+\cosh q_\parallel c+\frac{\alpha}{2}e^{q_\parallel c},$$

$$C\equiv G\sinh^2 q_\parallel c+1+\frac{\alpha}{2}, \tag{11}$$

with

$$G\equiv \tfrac{1}{2}[(b^2-1)^{-1/2}-1/\sinh q_\parallel c]/\sinh q_\parallel c,$$

$$H\equiv \tfrac{1}{2}[u^{-1}(b^2-1)^{-1/2}-e^{-q_\parallel c}/\sinh q_\parallel c]/\sinh q_\parallel c,$$

$$Q\equiv \tfrac{1}{2}[1-(b^2-1)^{-1/2}(1-b\cosh q_\parallel c)/\sinh q_\parallel c] - \tfrac{1}{2}\alpha e^{q_\parallel c}(b^2-1)^{-1/2}(\cosh q_\parallel c-b)/\sinh q_\parallel c, \tag{12}$$

where u and F are defined in Eq. (4) and now $b=\cosh q_\parallel c - v_{2D}E_+\sinh q_\parallel c$. The parameter $\alpha\equiv(\epsilon-\epsilon_0)/(\epsilon+\epsilon_0)$ depends on the optical dielectric constants (ϵ) inside and (ϵ_0) outside the superlattice. It plays a key role in determining the surface contributions as well as the appearance and energy of surface plasmons. The formula for α can be rewritten in the useful form $\epsilon/\epsilon_0=(1+\alpha)/(1-\alpha)$. We call attention to the similarity between the first term in Eq. (10) and the first term in Eq. (3). In the rhs of Eq. (10), the first term ($\equiv I_B$) gives the *bulk* contribution, while the second term ($\equiv I_S$) is associated with the *surface* contribution. The three poles mentioned earlier are exhibited by both contributions: $F=0$ corresponding to an in-phase plasmon which Raman scattering picks up and $b=\pm 1$ corresponding to the upper and lower limits of the bulk plasmon band. There is a *new* pole of the surface contribution I_S given by

$$Q(q_\parallel,\omega)=0, \tag{13}$$

which can be shown to correspond to a surface plasmon. One has a nontrivial solution of $Q=0$ only when $\alpha\neq 0$ (i.e., $\epsilon\neq\epsilon_0$); that is, the surface of the superconducting superlattice must separate regions with different dielectric constants to give rise to surface plasmons.[4]

In Fig. 2, we show the dispersion relation of surface plasmons in a superconducting superlattice, as given by the solutions of $Q=0$, for various values of α. The shaded area between the line denoted by $b=-1$ and the line $\omega=2\Delta$ represents the bulk plasmon band of an infinite superconducting superlattice. We find that the surface plasmon appears only above the upper limit (i.e., $\omega=2\Delta$) of this bulk plasmon band, where BCS particle-hole damping of collective modes can occur. For positive values of α ($\epsilon>\epsilon_0$), a surface plasmon appears at very large energies $\omega\gg 2\Delta$, in which case it is essentially identical to that in a normal superlattice. We remark that for a high-T_c material with a dielectric constant $\epsilon\sim 10$ in a vacuum ($\epsilon_0=1$), one has $\alpha=0.82$. For α increasingly negative ($\rightarrow -1.0$), which requires $\epsilon_0/\epsilon>1$, the surface plasmon energy slowly *decreases* toward 2Δ (see Fig. 2).

In Fig. 2, the dispersion relation denoted by $F=0$ represents a (bulk) plasmon, which is a pole of the Raman scattering intensity in Eq. (10). One sees that $F=0$ mode is well defined only when $q_\parallel\lesssim 0.025\Delta/v_F$ (solid line). The critical value of $q_\parallel$ ($0.025\Delta/v_F$) changes for different choices of δ and $k_\perp$. When $q_\parallel\gtrsim 0.025\Delta/v_F$, we find no solution for $F=0$. The dashed line represents the minima of F (i.e., an overdamped or relaxational mode). This broad resonance is always peaked at $\omega/2\Delta=0.8$, whatever the values chosen for δ and $k_\perp$.

In Fig. 3, we show the net Raman intensity based on (10) for a semi-infinite superconducting single-layer superlattice, showing the surface and the bulk components. Comparing Fig. 3 with Fig. 1, one sees that the low-frequency Van Hove singularity at $b=-1$ from the bulk contribution is canceled by the negative surface contribution. In contrast, the *in-phase* phase bulk plasmon mode ($F=0$) shows up as a sharp peak in the low-frequency region. As shown in Fig. 3, a peak associated with the $b=1$ Van Hove singularity can still appear at $\omega=2\Delta$ since the bulk and surface contributions do not completely cancel each other.

Figure 4 is similar to Fig. 3 using the same parameters, but at a much higher momentum transfer $q_\parallel=0.1\Delta/v_F$. The *cancellation* between the bulk and surface contributions is

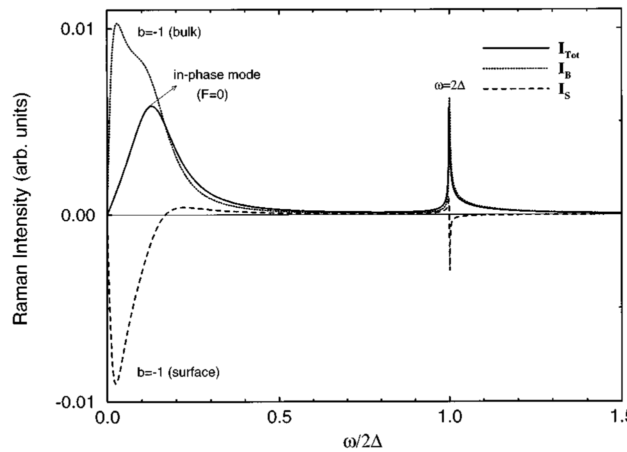

FIG. 3. Raman intensity given by Eq. (10) from both bulk (dotted line) and surface (dashed line) contributions for a semi-infinite superconducting superlattice. The same parameters are used as in Fig. 1, with $\alpha=0.82$ (corresponding to $\epsilon_0=1$ and $\epsilon=10$). Apart from the absence of the out-of-phase phase mode (only expected when the unit cell has two layers), the bulk contribution is very similar to that given in Fig. 1.

clearly shown, not only for the two boundaries of the bulk plasmon band at $b=-1$ and $\omega=2\Delta$, but almost for the entire region below 2Δ. We also see that at $q_\parallel=0.1\Delta/v_F$, the broad relaxational mode [always peaked at $\omega\approx 0.8(2\Delta)$] corresponding to the minimum of F (see Fig. 2) has a very low weight in the Raman-scattering spectrum.

To see how the interplay between the bulk and surface contributions depends on $q_\parallel$, we plot in Fig. 5 the *total* Raman intensities for various values of $q_\parallel$. Comparing Fig. 5 with Fig. 2, one finds that for $q_\parallel\lesssim 0.025\Delta/v_F$, a well-defined bulk plasmon mode ($F=0$) gives rise to a sharp peak even after the cancellation of the bulk and surface contributions. A peak associated with $\omega=2\Delta$ still shows up. As mentioned above, for $q_\parallel\gtrsim 0.025\Delta/v_F$, the minimum of F results in a very broad maximum at $\omega/2\Delta\approx 0.8$. We also note that for $q_\parallel\gtrsim 0.025\Delta/v_F$, while both the bulk and surface contribu-

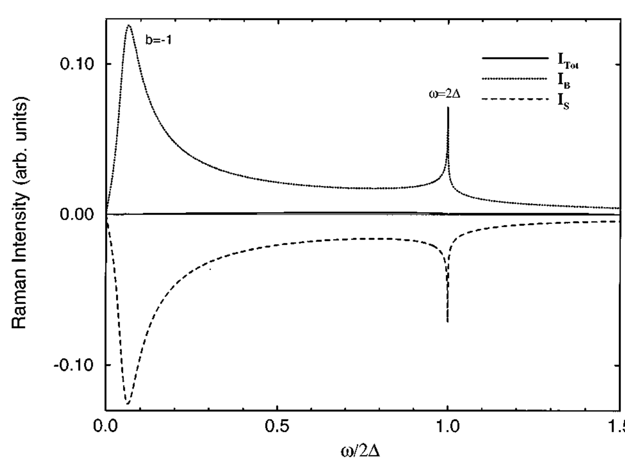

FIG. 4. Raman intensities as in Fig. 3 except for a much larger value $q_\parallel=0.1\Delta/v_F$. This plot clearly shows the almost complete mutual cancellation of the bulk and surface contributions at such large values of $q_\parallel$.

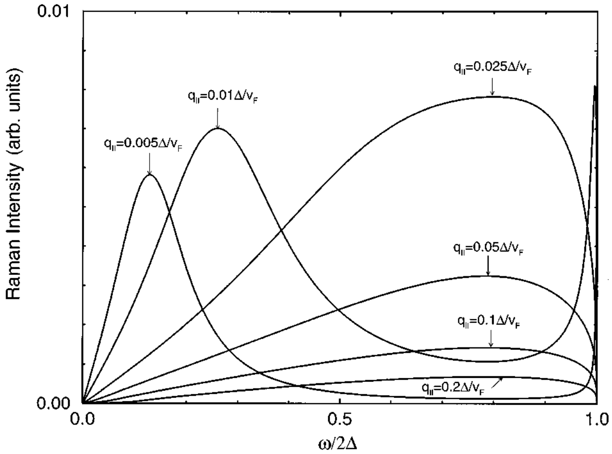

FIG. 5. The total Raman intensity in the region $\omega \leqslant 2\Delta$ (including *both* bulk and surface contributions) for various values of the momentum transfer $q_\parallel$. The peak is associated with the zero or minimum of F Eq. in (14).

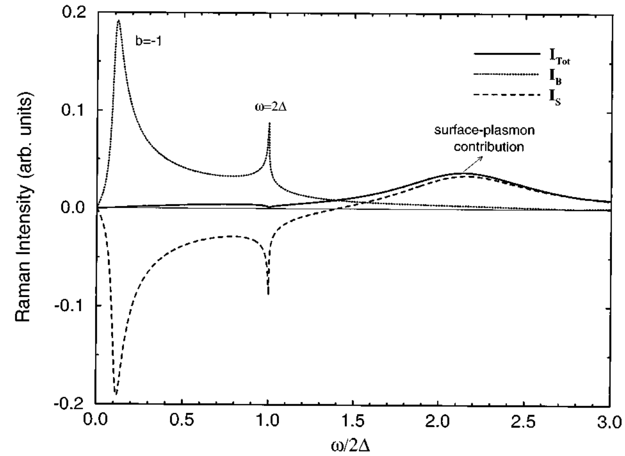

FIG. 6. The Raman intensity as in Fig. 3, with $q_\parallel = 0.2\Delta/v_F$ and $\alpha = -0.8$.

tions are roughly proportional to $q_\parallel^2$, the *net* weight after the mutual cancellation of bulk and surface contribution effectively *decreases* as $q_\parallel$ increases.

For c/δ, $q_\parallel c$, and $k_\perp c \ll 1$ appropriate for layered superconductors, the total Raman intensity given in Eq. (10) can be reduced after some calculation to

$$I(\omega) \simeq \frac{\delta}{2c} \mathrm{Im}\left(\frac{E_+}{F}\right)\left[\left(\frac{c}{\delta}\right)^2 + (2k_\perp c)^2\right], \qquad (14)$$

which is valid for $\overline{q_\parallel} \ll \overline{\omega} < 1$ and for all values of α. We note that in Eq. (14), the function F given in Eq. (4) is a very sensitive function of c/δ and $k_\perp c$ and therefore we cannot approximate it by $(u-1)^2$ in the limit of c/δ, $k_\perp c \to 0$. We can see directly from Eq. (14) that the poles of $b = \pm 1$ are removed as a consequence of the cancellation between bulk and surface contributions. The only pole now is given by $F=0$. One has a broad spectrum without any sharp peak for $q_\parallel \gtrsim 0.025\Delta/v_F$. In this region, one may verify that $F \propto E_+^2 \propto q_\parallel^4$. As a result, the net Raman intensity $I(\omega)$ decreases as $q_\parallel$ increases, roughly proportional to $q_\parallel^{-2}$ (see Fig. 5).

In addition to the surface contribution discussed above, there may be a surface plasmon in the region $\omega > 2\Delta$ (see Fig. 2) but this only arises when we have different dielectric constants inside and outside the superlattice ($\epsilon \neq \epsilon_0$). In Fig. 6, we show the contribution of a surface plasmon to the Raman intensity. The parameters used are as in Fig. 3 but at a much higher momentum transfer $q_\parallel = 0.2\Delta/v_F$ (which is probably the upper limit for Raman scattering in high-T_c superconductors). In order to have a surface plasmon energy fairly close to 2Δ, the dielectric constants are taken to give $\alpha = -0.80$. The latter value requires $\epsilon_0/\epsilon = 9$, i.e., a layered superconductor with a *much lower* dielectric constant compared to the overlay material. As shown in Fig. 6, this gives a Raman spectrum with lots of structure, with a broad surface plasmon peak at an energy above 2Δ. This region is the pair-breaking region, where there is strong BCS particle-hole damping of collective modes. The intensity of the surface plasmon is roughly proportional to $q_\parallel^2$. Once again, Fig. 6 shows the almost complete cancellation between the bulk and surface contributions in the region of $\omega \leqslant 2\Delta$. This is because at this relatively large value of $q_\parallel$, there is no well-defined solution of $F=0$ (see Fig. 2).

One might worry that the bilayer out-of-phase phase mode shown in Fig. 1 might also be strongly modified due to the surface contributions at higher values of $q_\parallel$. However, while the intensity (and the dispersion relation) of the out-of-phase phase mode is very sensitive to the pair tunneling strength T_J, it is not strongly dependent on the value of $q_\parallel$. It is associated with out-of-phase oscillation of order parameters in a single bilayer, with no *net* charge fluctuation.[1] Therefore, we do not expect any strong modification of the out-of-phase phase mode at larger values of $q_\parallel$.

IV. CONCLUSIONS

We have shown that the surface contribution plays a major role in determining the final Raman-spectrum line shape from semi-infinite superconducting superlattices. We find that, as in the case of normal superlattices discussed by Jain and Allen,[4] the proper inclusion of the surface contribution cancels ''spurious'' bulk contributions associated with Van Hove singularities (see Ref. 1) of the upper and lower limits of the bulk plasmon band of an infinite superconducting superlattice. We have also found that the bulk plasmon mode in the region $\omega < 2\Delta$ ceases to be well defined when $q_\parallel$ reaches a critical value ($\sim 0.025\Delta/v_F$ for the parameters we have used). In addition, the surface plasmon usually contributes to the Raman intensity in the region well *above* 2Δ and only approaches 2Δ if the superconductor is overlayed by a transparent material with a dielectric constant ϵ_0 much larger than that of the superlattice ϵ. The surface-plasmon mode intensity increases as $q_\parallel^2$ and thus one wants $q_\parallel$ as large as possible if one wants to study it (see Fig. 6).

As mentioned above, for relatively large values of $q_\parallel$, the (negative) surface contribution tends to completely cancel out the bulk contribution in the entire frequency region *below* 2Δ. Because the out-of-phase phase mode discussed in Ref. 1 is not expected to be strongly affected by the surface contribution, at relatively large values of $q_\parallel$, this mode (see

Fig. 1) should be the *only* structure remaining in the Raman spectrum below 2Δ.

The fact that the surface contribution cancels much of the bulk contribution can be understood in physical terms. The bulk contribution is based on response functions in Eq. (2) which are for an infinite superlattice. This ignores the surface ''reflections'' which will occur at the boundary of any semi-infinite system. These surface effects thus effectively remove correlations which are included in an infinite system, which is why they have a negative weight.

The absolute intensity of the Raman spectra we discuss in this paper is somewhat below current experimental sensitivity. However, we hope that the interesting predictions we make concerning the out-of-phase phase modes as well as surface plasmons will encourage future experimental efforts.

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[1] W. C. Wu and A. Griffin, Phys. Rev. B **52**, 7742 (1995).
[2] S. Chakravarty, A. Sudbø, P. W. Anderson, and S. Strong, Science **261**, 337 (1993).
[3] W. C. Wu and A. Griffin, Phys. Rev. B **51**, 15317 (1995).
[4] J. K. Jain and P. B. Allen, Phys. Rev. B **32**, 997 (1985).
[5] G. F. Giuliani and J. J. Quinn, Phys. Rev. Lett. **51**, 919 (1983).
[6] G. E. Santoro and G. F. Giuliani, Phys. Rev. B **37**, 8443 (1988).
[7] T. P. Devereaux and D. Einzel, Phys. Rev. B **51**, 16336 (1995).
[8] W. C. Wu, Ph.D. thesis, University of Toronto, 1996.
[9] R. Côté and A. Griffin, Phys. Rev. B **48**, 10404 (1993).
[10] H. A. Fertig and S. Das Sarma, Phys. Rev. B **44**, 4480 (1991).
[11] In this paper, all the Raman-scattering intensities are given using the same arbitrary units, with the *same* prefactors. Our unit corresponds to a few photon counts per second, which is roughly the threshold in current Raman experiments.