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Collective *d*-wave exciton modes in the calculated Raman spectrum of Fe-based superconductors

D. J. Scalapino
Department of Physics, University of California, Santa Barbara, California 93106-9530, USA

T. P. Devereaux
Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA
and Geballe Laboratory for Advanced Materials, Stanford University, California 94305, USA
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Calculations of the pairing interaction in multiband models of the Fe superconductors show that it is attractive in both the A_{1g} (*s*-wave) and B_{1g} (*d*-wave) channels. This raises the possibility that these materials may have collective excitonic modes. Here, assuming an *s*-wave ground state, we investigate the *d*-wave collective excitonic mode and its coupling to the Raman scattering.

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Both random-phase approximation (RPA) fluctuation exchange[1,2] and numerical functional renormalization-group (RG) calculations[3] find that *s*-wave (A_{1g}) and *d*-wave (B_{1g}) instabilities can occur in multiband models of the Fe-pnictides. Typically the pairing strength or T_c of the *s*-wave state[4] is found to be greater than that of the *d*-wave state. Nevertheless, there are parameter ranges where the two states lay relatively close, raising the possibility that there could be a *d*-wave (B_{1g}) collective excitonic mode.[5,6] In a fully gapped superconductor, this mode, consisting of two quasiparticles in a "Cooper pair" *d*-wave state, lays below 2Δ for zero center of mass momentum and would appear as a sharp peak. For the Fe superconductors, calculations suggest that the *s*-wave gap in the ground state is anisotropic and may even have nodes. In this case, the collective state could be damped and appear as a broad resonance in the two quasiparticle *d*-wave channel. Experimentally such a mode with angular momentum $L=2$ could be excited from an *s*-wave superconducting state by Raman scattering.[7] The observation of such a collective mode would provide evidence that there is an attractive pairing interaction in both the singlet A_{1g} and B_{1g} particle-particle channels with the A_{1g} being the strongest. This would support the results found in fluctuation-exchange calculations[1,2] of the pairing interaction for the Fe superconductors. Early microwave measurements found indications of a precursor response just below twice the superconducting gap Δ in Pb, and it was initially thought that this might be a *p*-wave collective mode. However, further studies determined that this was an artifact.[8] Here we explore the possibility of the existence of a *d*-wave collective mode in the Fe-pnictides and examine how it could be detected by Raman scattering.

We will begin by considering the simple case illustrated in Fig. 1(a). Here we imagine that the two-hole Fermi surfaces around the Γ point of the 1 Fe/cell Brillouin zone have been collapsed into one α Fermi sheet and β_1 and β_2 represent the two-electron Fermi sheets. Suppose the *s*-wave (A_{1g}) part of the pairing interaction connecting the α and β Fermi sheets is denoted by V with a cutoff ω_0 on $|\varepsilon_k|$ around the Fermi surfaces. There will of course also be $\beta_1-\beta_2$ contributions to the *s*-wave pair scattering as well as intra α, β_1 and β_2 terms which we neglect in this simple model. Then the A_{1g} pairing instability represented by the diagrams in Fig. 1(b) is determined from the BCS gap equations at T_c for the multisheeted Fermi surfaces shown in Fig. 1(a),[9]

$$-2\frac{T_c}{N}\sum_{kn} VG_{\beta_1}(k,i\omega_n)G_{\beta_1}(-k,-i\omega_n)\phi_{\beta_1}=\phi_\alpha \tag{1}$$

and

$$-\frac{T_c}{N}\sum_{kn} VG_{\alpha}(k,i\omega_n)G_{\alpha}(-k,-i\omega_n)\phi_{\alpha}=\phi_{\beta_1},$$

with $G_{\beta,\alpha}(k,i\omega_n)=[i\omega_n-\varepsilon_\beta(k)]^{-1}$ the single-particle Green's function on the β or α Fermi surfaces, V the $\alpha-\beta$ pairing interaction, and $\phi_{\beta,\alpha}$ the gap function amplitude on the β and α Fermi surfaces, respectively. From Eq. (1), the transition temperature is determined by

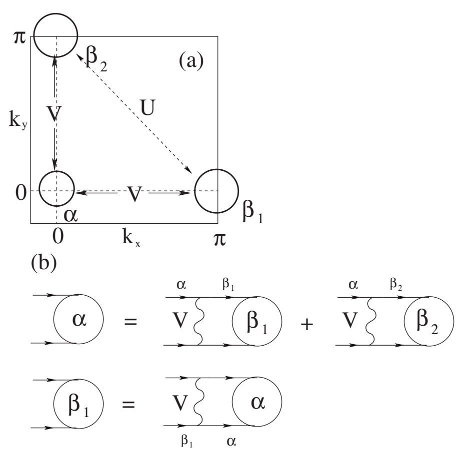

FIG. 1. (a) The Fermi surfaces in the 1 Fe/cell Brillouin zone. Here we have combined the α_1 and α_2 hole Fermi surfaces into one α sheet. For the simple example that we will consider the pairing interaction for the A_{1g} (*s*-wave) ground state is described by a strength V for scattering pairs between the α and β_1 and β_2 Fermi surfaces. The *d*-wave part of the interaction U scatters *d*-wave pairs between β_1 and β_2. (b) Diagrams for the A_{1g} pairing instability.

$$2N_\beta(0)N_\alpha(0)V^2\ln^2\left(\frac{2\gamma\omega_0}{\pi T_c}\right)=1, \tag{2}$$

with the s-wave coupling strength $\lambda_s=\sqrt{2N_\beta(0)N\alpha(0)}V$ and $\gamma\simeq 1.78$. The ratio of the gap amplitudes at T_c is

$$\frac{\phi_\alpha}{\phi_\beta}=-\sqrt{\frac{2N_\beta(0)}{N_\alpha(0)}}, \tag{3}$$

with N_α and N_β the density of states on the α and β Fermi surfaces, respectively.

In the superconducting state, the dominant d-wave scattering between the quasiparticles occurs between the β_1 and β_2 Fermi surfaces. We will parametrize the d-wave part of this interaction by the separable form

$$\Gamma^d(k,k')=-g^d_{\beta_1}(\theta)Ug^d_{\beta_2}(\theta')-g^d_{\beta_2}(\theta)Ug^d_{\beta_1}(\theta') \tag{4}$$

for $|\varepsilon_k|$ and $|\varepsilon_{k'}|$ less than a cut-off frequency ω_0. Here, $g^d_{\beta_i}(\theta)$ depends upon the angle of k on the β_i-Fermi surface measured from the k_x axis and $g^d_{\beta_2}(\theta)=-g^d_{\beta_1}(\theta+\pi/2)$.

Similarly to our treatment of the s-wave pairing channel, here for simplicity we will neglect $\beta-\alpha$ contributions to the d-wave channel. The additional contributions to both the s- and d-wave pairing interactions basically only change the strengths of the effective s- and d-wave pairing interactions λ_s and λ_d which we take as parameters in the following.

If the system were to remain in the normal state, supercooled below the s-wave pairing instability, it would become unstable to pairing in the d-wave channel when

$$1=\frac{U}{N}\sum_k g^d_\beta(k)^2\tanh\beta_c\varepsilon(k)/2$$

$$\simeq UN_\beta(0)\int\frac{d\theta}{2\pi}g^d_\beta(\theta)^2\ln\left(\frac{2\gamma\omega_0}{\pi T_c}\right). \tag{5}$$

Normalizing the angular average of $g^d_\beta(\theta)^2$ to unity around the β_1 Fermi surface, the d-wave transition temperature is

$$T_d\sim\omega_0 e^{-1/\lambda_d},$$

with the d-wave coupling strength $\lambda_d=N_\beta(0)U$. Fluctuation exchange calculations[1,2] and numerical renormalization-group studies[3] for models of the Fe superconductors find that the coupling strength λ_d can be comparable to the coupling strength in the s-wave channel λ_s, raising the possibility that one may find a d-wave "Cooper pair" collective mode in the s-wave superconducting state.

The homogeneous Bethe-Salpeter equation for a collective d-wave mode is illustrated in Fig. 2(a). Here $k=(\mathbf{k},i\omega_n)$ and $q=(\mathbf{q},i\omega_m)$. The single- and double-arrow lines denote the single-particle Green's function,

$$G(k)=\frac{i\omega_n+\varepsilon(k)}{(i\omega_n)^2-\varepsilon^2(k)-\Delta^2_\beta(k)}, \tag{6}$$

and Gor'kov's anomalous Green's function,

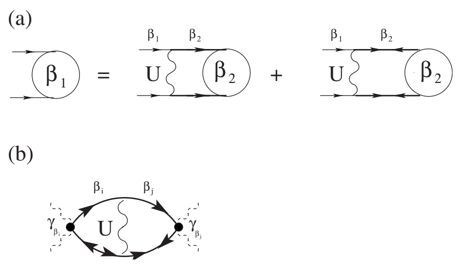

FIG. 2. (a) Diagrams for the d-wave collective mode. Here the thick single arrow line represents the single-particle Green's function $G(\mathbf{p},i\omega_n)$ and the double arrow line the Gor'kov anomalous Green's function $F(\mathbf{p},i\omega_n)$ in the A_{1g} state. (b) The lowest-order U contribution to the Raman scattering from interband pair interactions, scattering pairs between β_1 and β_2. Here γ_{β_i} is the Raman vertex on the β_i Fermi surface denoted by the solid circles.

$$F(k)=\frac{\Delta_\beta(k)}{(i\omega_n)^2-\varepsilon^2(k)-\Delta^2_\beta(k)}, \tag{7}$$

in the s-wave superconducting state, respectively, where Δ_β is the superconducting energy gap on band β. The Bethe-Salpeter equation for the d-wave collective mode is

$$\phi_q(k)=-\frac{T}{N}\sum_{k',n'}\Gamma^d(k,k')\times[G(k'+q)G(k')+F(k'+q)F(k')]\phi_q(k'). \tag{8}$$

For the separable interaction given by Eq. (4) one obtains an equation which determines the energy of the collective d-wave mode

$$1=U\frac{T}{N}\sum_{k'n'}[g^d_\beta(k')]^2\times[G(k'+q)G(k')+F(k'+q)F(k')]. \tag{9}$$

After the Matsubara sum is evaluated and $T\to 0$, we set $\mathbf{q}=0$ and analytically continue $i\omega_m\to\omega+i\delta$ to give

$$1=N_\beta(0)U\int\frac{d\theta}{2\pi}[g^d_{\beta_1}(\theta)]^2\int_{-\omega_0}^{\omega_0}\frac{d\varepsilon}{2}\frac{E}{E^2-(\omega/2)^2}, \tag{10}$$

with $E=\sqrt{\varepsilon^2+\Delta^2_\beta(\theta)}$ and ω is assumed to have a small positive imaginary part. Here $\Delta_\beta(\theta)$ is the s-wave ground-state gap on the β Fermi surface which we will set equal to $\Delta_0 g^s_\beta(\theta)$. The integral over ε is done in the usual way

$$\int_{-\omega_0}^{\omega_0}\frac{d\varepsilon}{2}\left(\frac{E}{E^2-(\omega/2)^2}-\frac{1}{E}\right)+\int_{-\omega_0}^{\omega_0}\frac{d\varepsilon}{2}\frac{1}{E}=\bar{P}(\omega,\theta)+\ln\left(\frac{2\omega_0}{\Delta_0(\theta)}\right) \tag{11}$$

and extending the range of integration for the first term to plus and minus infinity gives

$$\bar{P}(\omega,\theta) = \frac{[\omega/2\Delta_\beta(\theta)]}{\sqrt{1-[\omega/2\Delta_\beta(\theta)]^2}}\sin^{-1}\left[\frac{\omega}{2\Delta_\beta(\theta)}\right], \quad \frac{\omega}{|2\Delta_\beta(\theta)|} < 1 \; \frac{[\omega/2\Delta_\beta(\theta)]}{\sqrt{[\omega/2\Delta_\beta(\theta)]^2-1}}\left[\ln\left\{\left|\frac{\omega}{2\Delta_\beta(\theta)}\right| - \sqrt{\left[\frac{\omega}{2\Delta_\beta(\theta)}\right]^2-1}\right\} + i\frac{\pi}{2}\right], \quad \left|\frac{\omega}{2\Delta_\beta(\theta)}\right| > 1. \tag{12}$$

The collective d-wave mode at $q=0$ has a frequency and damping given by

$$\frac{1}{\lambda_d} - \frac{1}{\tilde{\lambda}_s} = \langle (g_\beta^d(\theta))^2 \bar{P}(\omega,\theta)\rangle, \tag{13}$$

where the bracket implies an angular average. Here the tilde s-wave coupling strength is

$$\frac{1}{\tilde{\lambda}_s} = \int \frac{d\theta}{2\pi}\ln\left(\frac{2\omega_0}{\Delta_0(\theta)}\right)(g_\beta^d(\theta))^2. \tag{14}$$

Depending on the difference in coupling strengths and the anisotropy of the s-wave gap on the β Fermi surfaces, one will have a sharp mode or a resonance.

A first-order contribution of the interaction vertex Γ^d to the Raman scattering is illustrated in Fig. 2(b).[10–13] There are four arrangements of the G and F propagators and one can go from β_1 to β_2 or β_2 to β_1. Finally adding the spin sum, the first-order contribution of Γ^d to the Raman susceptibility shown in Fig. 2(b) is

$$\Delta\chi(i\omega_m) = U(4\gamma_{\beta_1}GFg_{\beta_1}^d)(4g_{\beta_2}^d GF\gamma_{\beta_2}), \tag{15}$$

with

$$(4\gamma_\beta GFg_\beta^d) = 4\frac{T}{N}\sum_{k,n}\gamma_\beta(k)G(k+q)F(k)g_\beta^d. \tag{16}$$

Here $q=(\vec{q},i\omega_m)$ and we are interested in $\vec{q}=0$. Evaluating the Matsubara sum, we have

$$(4\gamma_\beta GFg_\beta^d) = N_\beta(0)\Delta_0\langle \gamma_\beta^d(\theta)g_\beta^d(\theta)g_\beta^s(\theta)\bar{P}(\omega,\theta)\rangle \tag{17}$$

and

$$\frac{\Delta\chi(\omega)}{N_\beta(0)} = -(N_\beta(0)U)\left(\frac{\Delta_0}{\omega}\right)^2 \times \langle \gamma_\beta(\theta)g_\beta^d(\theta)g_\beta^s(\theta)\bar{P}(\omega,\theta)\rangle^2. \tag{18}$$

Here again the bracket implies an angular average.

Symmetry considerations can be used to determine the collective mode contributions from the interplay of dominant and subdominant pair interactions and polarization geometries. From Eqs. (11), (12), (17), and (18), one can see from symmetry that the collective mode contribution to the Raman vertex will vanish unless $g_\beta^d\gamma_\beta g_\beta^s$ transforms as A_{1g} for tetragonal D^{4h} symmetry. As used here, since $g_\beta^s g_\beta^d$ transforms as one of the d-wave representation, a collective mode will appear only for crossed polarization incoming and scattered polarization geometries. Specifically, if one considers V to be in the $d_{x^2-y^2}$ channel, the collective mode will appear for B_{1g} orientations only. The possibility of a resonance in the A_{1g} Raman channel for a superconductor an s_{+-} gap has been recently discussed by Chubukov *et al.*[14]

As previously discussed, multiple scattering between the β_1 and β_2 Fermi surfaces leads to a collective d-wave Cooper pair state. Its contribution to the Raman scattering is obtained by replacing U in Eq. (15) with[10,11]

$$\frac{U}{1-N(0)UP(\omega)}. \tag{19}$$

Here

$$P(\omega) = \int\frac{d\theta}{2\pi}(g_\beta^d(\theta))^2\int_{-\omega_0}^{\omega_0}\frac{d\varepsilon}{2}\frac{E}{E^2-(\omega/2)^2}. \tag{20}$$

Proceeding as before, we find that

$$\frac{\text{Im}\,\chi(\omega)}{N_\beta(0)} = \text{Im}\left\{\frac{2\left\langle \gamma_\beta g_\beta^d\left(\frac{2\Delta_\beta(\theta)}{\omega}\right)\bar{P}(\omega,\theta)\right\rangle^2}{\left(\frac{1}{\lambda_d}-\frac{1}{\tilde{\lambda}_s}\right) - \langle (g_\beta^d)^2\bar{P}(\omega,\theta)\rangle}\right\}. \tag{21}$$

The lowest-order contribution to the β-Fermi surface Raman scattering is given by[12,13]

$$\frac{\text{Im}\,\chi_{\beta\beta}(\omega)}{N_\beta(0)} = \frac{4\pi}{\omega}\left\langle \frac{\gamma_\beta^2\Delta_\beta^2}{\sqrt{\omega^2-(2\Delta_\beta(\theta))^2}}\right\rangle. \tag{22}$$

If we set $(\gamma_\beta g_\beta^d)^2 = a\langle\gamma_\beta^2\rangle$ in Eqs. (21) and (22) we have the following expression for the Raman scattering:

$$\frac{\text{Im}\,\chi}{N_\beta(0)\langle\gamma_\beta^2\rangle} = \frac{4\pi}{\omega}\left\langle\frac{\Delta_\beta^2}{\sqrt{\omega^2-(2\Delta_\beta)^2}}\right\rangle + a\,\text{Im}\left\{\frac{2\left\langle\frac{2\Delta_\beta}{\omega}\bar{P}(\omega,\theta)\right\rangle^2}{\left(\frac{1}{\lambda_d}-\frac{1}{\tilde{\lambda}_s}\right) - \langle\bar{P}(\omega,\theta)\rangle}\right\}. \tag{23}$$

Here we have also set $\langle g_\beta^d(\theta)^2\rangle = 1$.

Figure 3 shows plots of $\text{Im}\,\chi/N_\beta(0)\langle\gamma_\beta^2\rangle$ for $\Delta_\beta(\theta) = \Delta_0(1+r\cos 2\theta)/(1+r)$ for various values of r and coupling strengths ($\tilde{\lambda}_s=1, \lambda_d=0.5$). The results indicate that the collective mode removes spectral weight from the higher-energy portion of the response and adds weight at the mode position determined by $1/\lambda_d - 1/\tilde{\lambda}_s$. For the isotropic gap ($r=0$), an essentially undamped mode appears below 2Δ, capturing most of the spectral weight from the bare contribution [the first term in Eq. (23)]. For a gap anisotropy $r=0.6$ that still preserves a true gap, a well-defined collective mode appears at frequencies slightly below $2\Delta_{\text{min}}$, removing the log singularity of the bare response at $2\Delta_{\text{max}}$ and shifting spectral weight to lower energies. For a gap with nodes ($r=1.4$), the collective mode is damped by the finite particle-hole continuum at all Raman energies and reallocates spectral weight to low energies near $|2\Delta_{\text{min}}|$.

For a stronger d-wave couplings $\lambda_d=0.8$, appropriate for the case of near-degenerate pair interactions, the collective

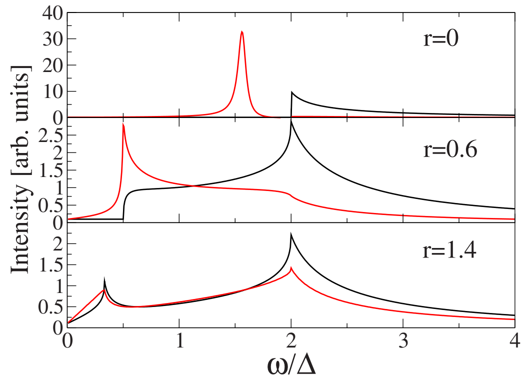

FIG. 3. (Color online) Plots of the Raman response for different gap anisotropies r in the absence of collective mode effects (black) and with collective contribution included (red or dark gray) for $\lambda_s=1$ and $\lambda_d=0.5$. Here the parameter a has been set to 1 and a small damping term has been added. Note the changes in scale of the $r=0$ plot.

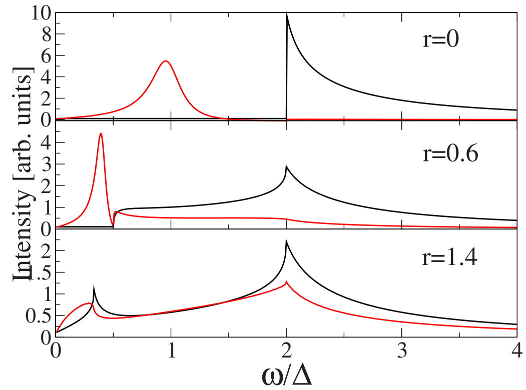

FIG. 4. (Color online) Same as Fig. 3 but for $\lambda_s=1$ and $\lambda_d=0.8$.

mode is pulled further away from the continuum contribution, as shown in Fig. 4. For the isotropic gap case, the mode drops to lower energies and has a smaller residue. This is the case for $r=0.6$ as well, where a well-defined collective mode pulls out of the continuum below $2\Delta_{\mathrm{min}}$. For the nodeful case $r=1.4$, the collective mode again drops to lower energies but remains damped. It however changes the low-frequency behavior of the Raman response considerably.

For the Fe-pnictides, contributions to the Raman response comes from each of the α and $\beta_{1,2}$ bands, plus mixing terms. As the d-wave collective mode contribution arises only from multiple scattering among the β bands, the contribution from the α bands will be determined from simple noninteracting considerations given in Ref. 13. For the case of degenerate $\beta_{1,2}$ bands having energy gaps $\Delta_{\beta_1,\beta_2}(\theta)=\Delta_0(1\pm r\cos 2\theta)/(1+r)$, respectively, the mixing terms vanish by symmetry for B_{1g} polarizations, and the collective mode contribution is twice Eq. (23), shown in Figs. 3 and 4.

Since the collective mode contribution is predicted to appear in crossed initial and scattered photon polarization orientations, this B_{1g} particle-particle mode will not be coupled to long-range Coulomb forces, which nominally push A_{1g} (parallel polarizations) collective mode contributions up in energy to the plasma particle-hole state. This may allow for this mode contribution to appear at low energies distinctly separate from the continuum in Raman experiments on the pnictides, unlike the situation in conventional superconductors.[8]

Therefore the detailed line shape of the electronic Raman continuum may be determined from the interplay of anisotropies of the Raman vertices and the structure of the pairing interaction using symmetry arguments as applied successfully in the cuprates.[10–12] What may distinguish the Fe pnictides from the cuprates may be the presence of pairing channels having almost equal strength as indicated in recent spin fluctuation and RG considerations. This Rapid Communication has shown that such a circumstance will result in collective mode contribution which will have an unique polarization signature in the Raman spectrum. This could open a window into the determination of the pairing structure of the pnictides and provide important clues to the pairing mechanism.

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