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Amplitude collective modes in superconductors and their coupling to charge-density waves

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At low temperature the long-wavelength perturbations of the amplitude of the superconducting gap propagate as an undamped collective mode with a finite frequency. The dispersion and damping of this mode are calculated. The phase or the Bogoliubov modes of a superconductor are strongly affected by Coulomb interactions and rendered indistinguishable from plasmons. By contrast, the amplitude modes are shown not to perturb the charge density thus remaining unaffected by the Coulomb interactions. Under certain conditions long-wavelength phonons couple to this mode. This coupling is derived and the observation of the amplitude mode through Raman scattering experiments in the charge-density-wave compound $NbSe_2$ are quantitatively explained.

I. INTRODUCTION

At long wavelengths and for temperatures close to the transition, the dynamics of the amplitude of the superconducting gap is given by the time-dependent Landau-Ginzburg equation.[1] This means that under these conditions the perturbations of the gap $\Delta(\vec{r},t)$ are overdamped. We show here that at low temperatures and long wavelengths there exists a well-defined mode associated with the variations of the gap. The frequency of this mode for $\vec{q}\rightarrow 0$ is 2Δ and in this limit it is undamped.

Unlike the mode of the phase of the superconducting order parameter (the Anderson-Bogoliubov mode),[2] the amplitude mode does not perturb the charge density and therefore is unaffected by Coulomb interactions. The amplitude mode, unlike the phase mode, therefore, remains *experimentally* relevant. We have investigated these modes in order to understand the result of Raman scattering experiments by Sooryakumar and Klein[3] (SK) on the superconductor—charge-density-wave (CDW) compound $NbSe_2$. In these experiments, the spectrum of certain phonons is investigated. We show how these phonons couple to the amplitude modes of the superconducting gap so that the latter are observable in a Raman experiment. We are also able to quantitatively explain the observations of SK using parameters obtained from a variety of experiments.

As is well known the phase mode in the superconducting state arises from consideration of gauge invariance.[4,5] This invariance is satisfied by the full Hamiltonian but not by the BCS reduced Hamiltonian. The amplitude mode may similarly be regarded as arising from the invariance of the full Hamiltonian to a certain local *nonunitary* transformation of the field operators first discussed by Nambu.[4] This transformation is sufficiently general so that perhaps well-defined amplitude modes exist corresponding to condensation of any sort. As an example, the familiar optical-phonon mode below a charge-density-wave transition may be derived from the general considerations with which we derive the amplitude mode in the superconductor.

Besides the phase or the Anderson-Bogoliubov modes, other collective modes for superconductors have been discussed. There are the excitonlike modes[5,6] for which no conclusive experimental evidence exist and the Carlson-Goldman modes[7] that have been observed in Al very near the transition temperature. The exciton modes may arise due to electron-electron attraction in angular-momentum channels other than that of the condensate. Carlson-Goldman modes are phase modes that are not pushed up to the plasma frequency because near the transition temperature the rate of conversion of normal↔superfluid fraction becomes very slow so that counterflow can maintain charge neutrality.[8] The amplitude modes for superconductors that we have investigated in this paper have been alluded to by Abrahams and Tsuneto.[1] To our knowledge no attention has been paid to them up to now, perhaps because of the lack of incentive from the experimental side. Several different collective modes[9] including the analog of the present one have been investigated in the context of anisotropic superfluidity in liquid ^3He. Modes similar to the amplitude mode discussed here first appeared in a paper by Nambu and Jona-Lasinio[10] in a dynamical symmetry-breaking theory of elementary particles. Recently this effort has been revived in the context of quantum chromodynamics and the σ meson has been identified as the analog of the amplitude mode discussed here.[11]

The simplest mechanical example of the phase and amplitude modes is the motion of a particle in a "jelly-mold"-shaped potential (see Fig. 1). There is no restoring force for motion around the potential valley (the analog of the phase mode), but we also expect radial oscillation of the ball at a finite frequency, which is the analog of the amplitude mode discussed here.

We shall first sketch the familiar calculation of the phase mode within the Nambu formalism (see, e.g., Ref. 4), because the derivation of the amplitude mode follows similar lines. A brief account of the present work has been published earlier.[12]

II. THE AMPLITUDE COLLECTIVE MODE IN SUPERCONDUCTORS

A. Model Hamiltonian

We consider a system of electron interacting via a nonretarded potential V; the Hamiltonian is

$$H_e=\sum_{k\sigma}\epsilon_k c^{\dagger}_{k\sigma}c_{k\sigma} +\tfrac{1}{2}\sum_{\substack{k'q\\ \sigma\sigma}} V(k,k',q)c^{\dagger}_{k+q\sigma}c^{\dagger}_{k'-q\sigma'}c_{k'\sigma'}c_{k\sigma}\ . \tag{2.1}$$

The potential $V(k,k',q)$, which is equal to $\langle k+q,k'-q\mid V\mid k,k'\rangle$, includes the electron-electron Coulomb repulsion as well as the attractive

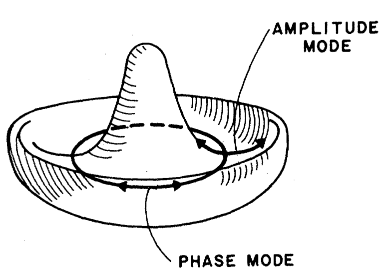

FIG. 1. Mechanical analog of a system described by a two-component parameter $\Delta e^{i\phi}$. The analog of the phase modes and amplitude modes are indicated.

interaction mediated by the phonons.

We use the Nambu formulation, where the electron creation and annihilation operators are written as two-component vectors,

$$\Psi_k=\begin{bmatrix} c_{k\uparrow}\\ c^{\dagger}_{-k\downarrow}\end{bmatrix},\quad \Psi^{\dagger}_k=(c^{\dagger}_{k\uparrow},c_{-k\downarrow})\ , \tag{2.2}$$

and the Hamiltonian (apart from constants) is rewritten as

$$H_e=\sum_{k}\epsilon_k\Psi^{\dagger}_k\tau_3\Psi_k +\tfrac{1}{2}\sum_{k'q}V(k,k',q) \times(\Psi^{\dagger}_{k+q}\tau_3\Psi_k)(\Psi^{\dagger}_{k'-q}\tau_3\Psi_{k'})\ . \tag{2.3}$$

The τ's are the Pauli matrices

$$\tau_1=\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix},\quad \tau_2=\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix},\quad \tau_3=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\ . \tag{2.4}$$

To obtain the results of BCS, one writes (2.3) in the form

$$H_e=H_0+H_1\ , \tag{2.5}$$

where H_0 is the BCS reduced Hamiltonian

$$H_0=\sum_k \Psi^{\dagger}_k(\tilde{\epsilon}_k\tau_3+\Delta\tau_1)\Psi_k\ , \tag{2.6}$$

and

$$\tilde{\epsilon}_k=\epsilon_k+\chi_k\ . \tag{2.7}$$

The propagator $G(k,\omega)$ for H_0 is

$$G(k,\omega)=\frac{\omega I+\tilde{\epsilon}_k\tau_3+\Delta\tau_1}{\omega^2-E_k^2\ i\delta}\ , \tag{2.8}$$

where

$$E_k^2=\tilde{\epsilon}_k^2+\Delta^2 \tag{2.9}$$

is the spectrum for quasiparticle excitations. Requiring the self-energy, shown in Fig. 2, to vanish gives the usual Hartree-Fock renormalization χ_k of the single-particle energies (which is the same in both normal and superconducting states and is therefore of no interest) as well as the BCS gap equation

$$\Delta_{k'}=-\int\frac{d^3k}{(2\pi)^3}\frac{\Delta_k}{2E_k}V_{kk'}\ . \tag{2.10}$$

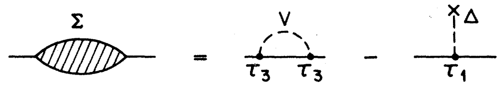

FIG. 2. Quasiparticle self-energy Σ with the BCS approximation.

B. Collective modes

1. The phase- (Bogoliubov) Anderson mode

In Eq. (2.6) the *phase* of the gap parameter has been arbitrarily chosen in the τ_1 direction in τ space. In fact, identical results for all physical properties should be obtained by choosing the phase to lie anywhere in the τ_1-τ_2 plane, i.e., for

$$\Delta\tau_1 \rightarrow \Delta(\tau_1\cos\alpha + \tau_2\sin\alpha) . \tag{2.11}$$

More generally, the results should be invariant to the gauge transformation

$$\Psi \rightarrow e^{i\alpha(r,t)\tau_3}\Psi, \quad \Psi^\dagger \rightarrow \Psi e^{-i\alpha(r,t)\tau_3} , \tag{2.21}$$

that leads to (2.11) for $\alpha(r,t)=$const. Satisfying gauge invariance ensures that in response to a longitudinal-electromagnetic perturbation, the continuity equation

$$\frac{\partial}{\partial t}(\Psi^\dagger\tau_3\Psi)+\vec{\nabla}\cdot\Psi^\dagger\frac{\vec{P}}{m}\Psi=0 \tag{2.13}$$

or

$$\sum_\mu q_\mu J_\mu = 0 \tag{2.14}$$

is satisfied. Here J_μ is the expectation value of the four-current operator:

$$J_\mu(q)=\sum_p \Psi_p^\dagger \gamma_\mu(p+q,p)\Psi_{p+q} , \tag{2.15}$$

$$\gamma_\mu(p+q,p)=\begin{cases}\tau_3 \quad (\mu=0)\\ \dfrac{1}{m}(p_i+\tfrac{1}{2}q_i) \quad (\mu=i=1,2,3) .\end{cases} \tag{2.16}$$

The BCS theory makes a specific choice of phase, and therefore does not satisfy the continuity equation in response to a longitudinal-field perturbation, whereas the full Hamiltonian H_0+H_1 does. To obtain the correct linear response, one must consider the modification of the vertex γ to the same order as the modification of the propagator. The relation between the modified vertex Γ and the propagator is given by the Ward identity

$$\Gamma_\mu=\gamma_\mu+\frac{\partial\Sigma}{\partial\vec{A}_\mu} , \tag{2.17}$$

where $\vec{A}$ is the vector potential of an external field. An approximation which satisfies the Ward identity (and hence the continuity equation) is the integral equation

$$\Gamma(k+q,k)=\gamma(k+q,k) + i\int \tau_3 G(k'+q)\Gamma(k'+q,k') \times G(k')\tau_3 V_{kk'}\frac{d^4k'}{(2\pi)^4} . \tag{2.18}$$

This is shown in Fig. 3 and is simply the sum of ladder diagrams generated by the residual interaction H_1.

The electromagnetic field couples to the electronic charge density $\Psi^\dagger\tau_3\Psi$. Taking $\gamma=\tau_3$, Eq. (2.18) has the solution

$$\Gamma(k+q,k)\approx\tau_3+\frac{2i\Delta\tau_2 q_0}{q_0^2-\alpha^2q^2} , \tag{2.19}$$

where $\alpha^2=\frac{1}{3}v_F^2$, with v_F the Fermi velocity. This shows that associated with a charge-density perturbation (neglecting the Coulomb interactions) the phase of the superconductor propagates as a collective mode with dispersion relation

$$q_0=\alpha q . \tag{2.20}$$

This is as it should be since the variation of the phase of the gap reads to a supercurrent. The dispersion relation for the phase collective mode can be easily obtained from Eq. (2.18) by looking for solutions of the homogeneous equation with $\gamma=0$, and $\Gamma=\phi(q_0,\vec{q})\tau_2$.

The relation between the continuity equation and the integral equation for the vertex can be seen from the fact that if we put

$$\gamma=G_0^{-1}(p+q)\tau_3-\tau_3G_0^{-1}(p) = \sum_\mu q_\mu\gamma_\mu(p+q,p) , \tag{2.21}$$

where γ_μ is the bare charge-current operator [Eq. (2.16)] and G_0 is the propagator in the absence of superconductivity, then (2.18) has the exact solution

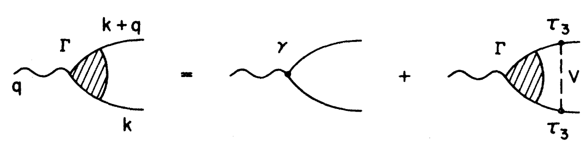

FIG. 3. Renormalization of the vertex Γ by the residual interaction H_1.

$$\Gamma = G^{-1}(p+q)\tau_3 - \tau_3 G^{-1}(p) = \sum_\mu q_\mu \Gamma_\mu(p+q,p) \; . \qquad (2.22)$$

Taken between two quasiparticle states, matrix elements of (2.22) are zero and thus the continuity equation for the "dressed" quasiparticle states is satisfied.

2. *Amplitude mode*

We have sketched the familiar calculation for the phase mode because in calculating the behavior of the amplitude mode we shall follow a similar procedure. Suppose we are interested in the response to a perturbation that directly couples to the magnitude of the gap; i.e., the vertex in τ space is proportional to τ_1. The signature of a collective amplitude mode will be that there exists a solution of the homogeneous version of (2.18) with $\gamma=0$, $\Gamma=\phi(q)\tau_1$ along some line $q_0(\vec{q})$ that is the mode dispersion relation. Thus we look for solutions of

$$\phi(q)\tau_1 = -V\int \tau_3 G(k+q)\phi(q)\tau_1 G(k)\tau_3 \times \frac{d^4k}{(2\pi)^4} \; , \qquad (2.23)$$

where we have assumed $V_{kk'}=-V$ in the separable BCS form. Provided $qv_F \ll \Delta$, and with the assumption of particle-hole symmetry, the right-hand side (rhs) of (2.23) is proportional to τ_1 and we can perform the frequency integral to obtain (hereafter $q_0=\nu$)

$$1+\tfrac{1}{2}V\int \frac{d^3k}{(2\pi)^3}\frac{E+E'}{EE'}\frac{EE'+\epsilon\epsilon'-\Delta^2}{\nu^2-(E+E')^2+i\delta}=0 \qquad (2.24)$$

with the notation $\epsilon_k=\epsilon$, $\epsilon'=\epsilon_{k+q}$, etc. We notice that in the limit $\vec{q}=0$, Eq. (2.24) becomes

$$1+\tfrac{1}{2}V\int \frac{d^3k}{(2\pi)^3}\frac{\epsilon^2}{E(\nu^2/4-E^2)}=0 \; . \qquad (2.25)$$

When $\nu=2\Delta$, this reduces to the gap equation (2.10) that is satisfied, and we deduce that there exists a collective mode with a mass 2Δ in the long-wavelength limit.

In order to determine the dispersion relation at long wavelengths we make use of the gap equation to write (2.24) in the form

$$\tfrac{1}{4}V\int \frac{d^3k}{(2\pi)^3}\frac{E+E'}{EE'}\frac{\nu^2-(\epsilon'-\epsilon)^2-4\Delta^2}{\nu^2-(E+E')^2}=0 \; . \qquad (2.26)$$

Some care must be exercised at this point because if we set $\nu=2\Delta$, $\vec{q}=0$, then the integrand in (2.39) contains a term $1/\epsilon_k^2$ leading to a divergent integral, while the numerator is zero. However, in the limit $\nu\to 2\Delta$, $\vec{q}=0$, the integral is well defined, and to order q^2 we obtain

$$\int \frac{d^3k}{(2\pi)^3}\frac{\nu^2-(\epsilon'-\epsilon)^2-4\Delta^2}{E(\nu^2-4E^2)}=0 \; . \qquad (2.27)$$

Performing the angular integral leads to

$$(\nu^2-4\Delta^2-\tfrac{1}{3}v_F^2q^2)J=0 \; , \qquad (2.28)$$

where the integral J is given by

$$J=N(0)V\int_0^{\omega_c} d\epsilon \frac{1}{E(\nu^2-4E^2)} \qquad (2.29)$$

with $N(0)$ the electronic density of states and ω_c the cutoff (Debye) frequency. Equation (2.29) is easily evaluated, and with $\omega_c \gg \Delta$, we have

$$J=\frac{N(0)V}{2[(\nu^2-4\Delta^2)]^{1/2}}\frac{1}{\nu}\ln\left|\frac{\nu+[(\nu^2-4\Delta^2)]^{1/2}}{\nu-[(\nu^2-4\Delta^2)]^{1/2}}\right| \qquad (2.30)$$

$$\simeq \frac{N(0)V}{4\Delta^2} \text{ for } \nu \gtrsim 2\Delta \; . \qquad (2.31)$$

Thus the dispersion relation for the amplitude mode is

$$\nu_q^2 = 4\Delta^2+\tfrac{1}{3}v_F^2q^2 \; . \qquad (2.32)$$

Since the frequency at finite q moves up into the continuum of quasiparticle states, the mode will be damped, i.e., ν is complex. This corresponds to the fact that (2.24) has an imaginary part for $\nu > 2\Delta$. We write (2.24) formally as

$$1+VK(\vec{q},\nu_q-i\gamma_q)=0 \; , \qquad (2.33)$$

and separating the real and imaginary parts (assuming $\gamma_q \ll \nu_q$) we obtain

$$\gamma_q = \mathrm{Im}K(q,\nu_q)\left[\left.\frac{\partial \mathrm{Re}K(q,\nu)}{\partial\nu}\right|_{\nu=\nu_q}\right]^{-1} , \qquad (2.34)$$

where ν_q is given by Eq. (2.32). From (2.31) we have

$$\left.\frac{\partial \mathrm{Re}K(\vec{q},\nu)}{\partial\nu}\right|_{\nu=\nu_q} \simeq \frac{N(0)}{\Delta} \; , \qquad (2.35)$$

while the imaginary part is

$$\text{Im}K=\frac{\pi}{4}\int\frac{d^3k}{(2\pi)^3}\frac{EE'+\epsilon\epsilon'-\Delta^2}{EE'}\times\delta(\nu-(E+E')) \quad (2.36)$$

$$=\frac{\pi^2N(0)}{2}\frac{(\nu-2\Delta)}{v_Fq} . \quad (2.37)$$

We obtain

$$\gamma_q=\frac{\pi^2}{24}v_Fq , \quad (2.38)$$

and consequently the mode will be overdamped for $qv_F/\Delta \gtrsim 1$.

The $T=0$ calculations presented here are actually valid at finite temperatures as long as quasiparticle lifetimes are long. The latter vary at low temperatures as $\exp(\Delta/k_BT)$. Near the transition temperature the collisionless limit in which the present calculations are performed is no longer valid, and the mode becomes overdamped. The amplitude of the superconducting gap is then describable by a time-dependent Landau-Ginzburg equation.

3. *Invariance relations*

The existence of the amplitude mode is related to a transformation property of the Hamiltonian in the same way as the phase mode was seen to be related to the charge-continuity equation. If we assume a bare vertex of the form

$$\gamma=G_0^{-1}(p+q)\tau_1+\tau_1G_0^{-1}(p) , \quad (2.39)$$

then the solution of (2.18) is exactly

$$\Gamma=G^{-1}(p+q)\tau_1+\tau_1G^{-1}(p) . \quad (2.40)$$

The existence of these exact solutions is a consequence of the invariance of the full Hamiltonian (2.3) to the nonunitary transformation

$$\Psi\rightarrow e^{\alpha\tau_1}\Psi,\quad \Psi^\dagger\rightarrow\Psi^\dagger e^{\alpha\tau_1} , \quad (2.41)$$

and simultaneously changes the gradient operator by

$$\vec{\nabla}\rightarrow\vec{\nabla}+\alpha\tau_1 .$$

The invariant is most easily seen by writing the Hamiltonian in real space

$$H=\int\vec{\nabla}\Psi^\dagger(\vec{r})\tau_3\nabla\Psi(\vec{r}) +\int V(\vec{r},\vec{r}\,')\Psi^\dagger(\vec{r})\tau_3\Psi(\vec{r})\times\Psi^\dagger(\vec{r}\,')\tau_3\Psi(\vec{r}\,') .$$

If the Lagrangian

$$L=\int\Psi^\dagger\frac{\partial}{\partial t}\Psi-H$$

is required to be invariant under an infinitesimal version of the transformation (2.41), one gets the "continuity" equation

$$i\Psi^\dagger\tau_i\left[\frac{\vec{\partial}}{\partial t}-\frac{\overleftarrow{\partial}}{\partial t}\right]\Psi+\vec{\nabla}\cdot\Psi^\dagger\tau_2\left[\frac{\vec{\mathrm{P}}}{m}+\frac{\overleftarrow{\mathrm{P}}}{m}\right]\Psi=0 . \quad (2.42)$$

This is precisely the procedure by which one gets the usual continuity equation (2.13) except that one uses the gauge (unitary) transformation (2.12). With the use of the definitions of (2.39) and (2.40), Eq. (2.42) becomes

$$\Psi^\dagger\gamma\Psi=0 , \quad (2.43)$$

where Ψ is the true Heisenberg operator. Thus the Ward identity (2.40) guarantees that Eq. (2.42) will be satisfied in the quasiparticle picture. Equation (2.42) can be interpreted in a straightforward manner as a "pseudocontinuity equation" for the Cooper-pair density. The current operator for Cooper pairs is

$$j_\mu^c(q)=\sum_k\Psi_k^\dagger\gamma_\mu^c(k+q,k)\Psi_{k+q} , \quad (2.44)$$

where

$$\gamma_\mu^c(k+q,k)=\begin{cases}\tau_1, & \mu=0\\ -i/2mq_i\tau_2, & \mu=i=1,2,3\end{cases} \quad (2.45)$$

and Eq. (2.39) becomes

$$\gamma=\sum_\mu(2k_\mu+q_\mu)\gamma_\mu^c(k+q,k) . \quad (2.46)$$

As pointed out by Nambu, there exist two other continuity equations that follow from requiring the invariance of the Lagrangian under infinitesimal transformation of the form

$$\Psi\rightarrow e^{i\alpha(x)}\Psi,\quad \Psi^\dagger\rightarrow\Psi^\dagger e^{i\alpha(x)} , \quad (2.47)$$

and

$$\Psi\rightarrow e^{\tau_2\alpha(x)}\Psi,\quad \Psi^\dagger\rightarrow\Psi^\dagger e^{\tau_2\alpha(x)} . \quad (2.48)$$

There exist Ward identities corresponding to both these transformations, that are of the form (2.21),(2.22) and (2.39),(2.40), viz,

$$\gamma=G_0^{-1}(p+q)-G_0^{-1}(p) ,\qquad \Gamma=G^{-1}(p+q)-G^{-1}(p) , \quad (2.49)$$

and

$$\gamma = G_0^{-1}(p+q)\tau_2 + \tau_2 G_0^{-1}(p)\ ,$$
$$\Gamma = G^{-1}(p+q)\tau_2 + \tau_2 G^{-1}(p)\ . \tag{2.50}$$

However, either of these lead to any new collective modes, since $\gamma = \Gamma$ in each case.

4. Coulomb effects

We have so far considered only neutral superconductors, and the inclusion of long-range Coulomb interactions is well known to have important consequences for the phase mode.[2,4] Including the screening of the vertex by the Coulomb potential $V_c(q) = 4\pi e^2/q^2$ leads to an extra term on the rhs of the vertex equation (2.18) (see Fig. 4), which is

$$-iV_c(q)\tau_3 \int \mathrm{Tr}[\tau_3 G(k+q)\Gamma(k+q,k)G(k)] \frac{d^4k}{(2\pi)^4} \tag{2.51}$$

With Γ proportional to τ_2 or τ_3, the integral is finite and thus (2.51) is proportional to $1/q^2$, which diverges. The next result is that the phase mode is pushed up to high energy and becomes the plasma oscillation of the electron gas, that is the same in both superconducting or normal metals.

For the amplitude mode, we set $\Gamma = \phi\tau_1$ as in (2.23), and (2.51) becomes

$$-iV_c(q)\tau_3 \int \frac{d\omega\, d^3k}{(2\pi)^3} \frac{2\Delta(\epsilon+\epsilon')}{(\omega^2 - E^2)[(\omega+\nu)^2 - E'^2]}\ , \tag{2.52}$$

which is zero if there is particle-hole symmetry, and hence Coulomb interactions produce no renormalization of the τ_1 (amplitude) mode. This is to be expected because the charge $\Psi^\dagger\tau_3\Psi$ is invariant under the transformation (2.41) and there is no coupling between the charge density and fluctuations in the amplitude of the gap.

5. Amplitude modes in other states

We see that there exist two distinct collective modes in a superconductor which correspond to fluctuations in the phase and amplitude of the gap. We believe that this is a quite general result for any system which undergoes a condensation into a state described by a two-component order parameter. A familiar example of this behavior is provided by an incommensurate charge-density-wave (CDW) state,

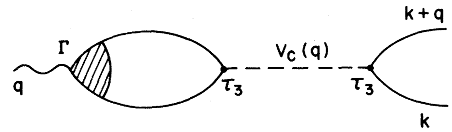

FIG. 4. Screening of the vertex via the Coulomb potential V_c in a charged superconductor.

where the order parameter is the induced charge density at wave vector q, of the form

$$\rho\cos(\vec{q}\cdot\vec{r}+\phi)\ . \tag{2.53}$$

For an incommensurate CDW, $\vec{q}$ bears no relation to the reciprocal-lattice vector, and hence the total energy is invariant under a change of the phase ϕ. This leads to the existence of a phase mode with an acoustic dispersion relation. There exists also a mode corresponding to the fluctuation of the amplitude ρ, that in this case is simply an optic phonon. The dispersion relation for the CDW phase and amplitude modes has been derived before by Lee, Rice, and Anderson.[13] These modes can be derived in a precisely analogous fashion to the superconducting amplitude and phase modes.[14]

A similar analysis also reveals that an amplitude mode exists at low temperatures also in materials with a condensed spin-density wave. The analog of the phase mode in that case is, of course, the spin-wave mode.

III. INTERACTION WITH PHONONS IN CDW MATERIALS

The superconducting amplitude mode is not directly observable in normal superconductors or ^{3}He-*B* because there is no coupling to charge fluctuations as we discussed in Sec. II B 4; its observation requires a field which couples to the electrons via the τ_1 vertex.

A. Deduction of the interaction Hamiltonian

In CDW materials there is such a coupling between the electrons and the soft-phonon mode describing the phase transition from the CDW to normal state as we have discussed earlier in a brief note.[12] The layer compound 2*H*-$NbSe_2$ undergoes a transition from the normal state into a slightly incommensurate CDW state at $T_d = 33$ K, and becomes superconducting below $T_c = 7.2$ K. Measurements of the charge of T_c and T_d with pressure have demonstrated that there is a coupling between the amplitude of the CDW lattice distortion and the superconducting gap.[15] As the hydrostatic pressure is increased from zero, the superconducting transition temperature rises while the CDW transition temperature falls. At around 35 kbar, T_d falls below T_c, and for higher pressures up to 140 kbar, T_c is almost independent of pressure.

It was argued[15] that this phenomenon can be understood by considering the effect of the amplitude of the CDW lattice distortion on the density of states at the Fermi level, which determines the superconducting transition temperature T_c. In the CDW state, a gap opens up over part of the Fermi surface in the direction of the q vectors of the CDW. This reduces the average density of states at the Fermi surface $N(0)$, and tends to lower T_c below the value expected for a non-CDW sample. As T_d decreases under pressure, the amplitude of the CDW lattice distortion u_0 will also decrease, thereby gradually restoring the Fermi surface and increasing T_c as well as the BCS gap parameter Δ.

The CDW phase transition is accompanied by the softening of a phonon mode. Below the transition, this phonon becomes frozen with an amplitude $\vec{u}_0$. However there still remains a time-dependent oscillation about this nonzero equilibrium value, i.e., $u(t)=u_0+u_1(t)$. The mode corresponding to $u_1(t)$ is a $q\simeq 0$ optic phonon with the same symmetry as the distortion u_0 and is often referred to as the amplitude mode of the CDW (CDW-AM). Keeping in mind that u_0 is coupled to the BCS gap Δ, the CDW amplitude mode will produce a time-dependent modulation of Δ. Thus the electron-phonon coupling for this mode will be of the form

$$H^{\Delta}_{e\text{-ph}}=g_q^{(\Delta)}(b_q+b^{\dagger}_{-q})\sum_k \Psi^{\dagger}_k\tau_1\Psi_{k+q} , \tag{3.1}$$

where $b,b^{\dagger}$ are annihilation and creation operators for the phonon amplitude mode, with $q\simeq 0$. Because the coupling occurs through the gap parameter Δ, the vertex is of τ_1 symmetry. For completeness, we also include the more conventional coupling through the charge vertex τ_3, although we shall see later that this does not lead to any important effects. Thus

$$H^{\rho}_{e\text{-ph}}=g_q^{(\rho)}(b_q+b -q^{\dagger})\sum_k \Psi^{\dagger}_k\tau_3\Psi_{k+q} . \tag{3.2}$$

Strictly there are two amplitude modes of different symmetry and so we should include two separate couplings in (3.1) and (3.2). However, the data do not allow us to extract separate values of the coupling constants for each symmetry type, and so we shall use a model with only a single CDW amplitude mode.

In order to estimate the value of $g^{(\Delta)}$, we make use of the measurements of T_c and T_d under pressure referred to earlier.[15] We assume that BCS gap Δ is described by

$$\Delta(p)=\Delta_0+\Delta_1\chi(p) \tag{3.3}$$

as a function of pressure p at $T=0$, where

$$\chi(p)=u_0(p)-u_0(p=0) \tag{3.4}$$

described the variation of the CDW lattice distortion with pressure. Thus we have

$$g^{\Delta}_{q=0}=\Delta_1(\hbar/2NM\omega_0)^{1/2} , \tag{3.5}$$

with N the number density of unit cells, M the reduced mass, and ω_0 the frequency of the phonon-amplitude mode.

We assume $T_d \,\alpha\, u_0^2$ $(T=0)$ which is a general property of a mean-field-like second-order transition. From the pressure data, we have

$$\frac{\partial T_c}{\partial T_d}\sim\left.\left[\frac{\partial T_c}{\partial p}\Big/\frac{\partial T_d}{\partial p}\right]\right|_{p=0}\simeq -0.15 , \tag{3.6}$$

and using the BCS result $\Delta=1.76k_aT_c$ we obtain

$$\Delta_1\simeq -0.5\frac{k_BT_d}{u_0} . \tag{3.7}$$

We define a dimensionless coupling constant

$$\alpha=\frac{4g^{(\Delta)^2}N(0)}{\hbar\omega_0}\frac{1}{\lambda^2} , \tag{3.8}$$

with

$$\lambda=N(0)V=[\ln(2\hbar\omega_0/\Delta)]^{-1}\simeq 0.3 . \tag{3.9}$$

The density of states $N(0)$ is estimated from the width of the lowest d band from band-structure calculations to be $\sim 1.5\ (\text{eV})^{-1}$ per Nb.[16] We find

$$\alpha\simeq 5\times 10^{-5}/u_0^2\ (\text{Å}) . \tag{3.10}$$

The atomic displacement u_0 has not been measured for $2H$-$NbSe_2$, but in $2H$-$TaSe_2$ it was found to be $\simeq 0.025$ Å, and in $2H$-$NbSe_2$ it is estimated to be about $\frac{1}{2}$ to $\frac{1}{3}$ of this, bearing in mind the factor-of-4 lowering of T_c.[17] As a rough estimate, we obtain

$$\alpha\simeq 0.3-0.6 . \tag{3.11}$$

B. Calculation of the phonon self-energy

The full Hamiltonian is now given by

$$H = H_e + H_{e\text{-ph}} + H_{\text{ph}} , \tag{3.12}$$

with H_e given by (2.5), $H_{e\text{-ph}}$ by (3.1) and (3.2), and

$$H_{\text{ph}} = \hbar\omega_0 b_q^\dagger b_q \tag{3.13}$$

is the phonon part of the Hamiltonian describing the CDW amplitude mode. We restrict our discussion to $\vec{q}=0$, and we are interested in calculating the self-energy of the CDW amplitude mode in order to determine its spectral weight. Owing to the presence of the superconducting amplitude collective mode at a frequency close to the BCS gap 2Δ, we may expect that the coupling term H^Δ in the τ_1 vertex will introduce a structure in the phonon spectral weight $S(\nu)$ for $\nu \sim 2\Delta$. However, to obtain this result we must perform the vertex renormalization that we discussed in Sec. II.

We write the Dyson equation for the phonon propagator $D(\nu, q \simeq 0)$ as

$$D^{-1}(\nu) = D_0^{-1}(\nu) - \Pi(\nu) . \tag{3.14}$$

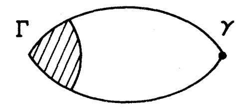

FIG. 5. Self-energy Π of an external field interacting with a superconductor.

The phonon self-energy including vertex corrections is given by (see Fig. 5)

$$\Pi(\nu) = -i \int \text{Tr}[\gamma G(\vec{k}, \omega+\nu)\Gamma(\nu)G(\vec{k},\omega)] \times \frac{d^3k\, d\omega}{(2\pi)^4} , \tag{3.15}$$

where we have taken $q=0$, $\nu \neq 0$, and

$$\gamma = g^{(\Delta)}\tau_1 + g^{(\rho)}\tau_3 , \tag{3.16}$$

and $\Gamma(\nu)$ can be calculated by solving the integral equation (2.18). If we ignore this vertex renormalization and set $\Gamma=\gamma$, we obtain

$$\Pi(\nu) = \Pi_0^\Delta(\nu) + \Pi_0^\rho(\nu) , \tag{3.17}$$

where

$$\Pi_0^\Delta(\nu) = -i(g^\Delta)^2 \int \text{Tr}[\tau_1 G(\vec{k},\omega+\nu)\tau_1 G(\vec{k},\omega)] \frac{d^3k\, d\omega}{(2\pi)^4} , \tag{3.18}$$

$$\Pi_0^\rho(\nu) = -i(g^\rho)^2 \int \text{Tr}[\tau_3 G(\vec{k},\omega+\nu)\tau_3 G(\vec{k},\omega)] \frac{d^3k\, d\omega}{(2\pi)^4} . \tag{3.19}$$

Equations (3.18) and (3.19) can be readily evaluated and we obtain

$$\text{Re}\Pi_0^\Delta(\nu) = \begin{cases} -2N(0)g^{(\Delta)^2}\left[\lambda^{-1} - \left[\dfrac{4\Delta^2-\nu^2}{\nu^2}\right]^{1/2} \tan^{-1}x\right] & \text{for } \nu < 2\Delta \\ -2N(0)g^{(\Delta)^2}\left[\lambda^{-1} - \dfrac{1}{2}\left[\dfrac{\nu^2-4\Delta^2}{\nu^2}\right]^{1/2} \ln\left|\dfrac{1+x}{1-x}\right|\right] & \text{for } \nu > 2\Delta \end{cases} \tag{3.20}$$

$$\text{Im}\Pi_0^\Delta = \begin{cases} 0, & \nu < 2\Delta \\ -\pi g^{(\Delta)^2} N(0)\left[\dfrac{\nu^2-4\Delta^2}{\nu^2}\right]^{1/2}, & \nu > 2\Delta \end{cases} \tag{3.21}$$

$$\text{Re}\Pi_0^\rho(\nu) = \begin{cases} -8g^{(\rho)^2}N(0)\dfrac{\Delta^2}{\nu(4\Delta^2-\nu^2)^{1/2}}\tan^{-1}x & \text{for } \nu < 2\Delta \\ -4g^{(\rho)^2}N(0)\dfrac{\Delta^2}{\nu(\nu^2-4\Delta^2)^{1/2}}\ln\left|\dfrac{1+x}{1-x}\right| & \text{for } \nu > 2\Delta \end{cases} \tag{3.22}$$

$$\text{Im}\Pi_0^\rho(\nu) = \begin{cases} 0, & \nu < 2\Delta \\ -\dfrac{4\pi g^{(\rho)^2}N(0)\Delta^2}{\nu(\nu^2-4\Delta^2)^{1/2}}, & \nu > 2\Delta \end{cases} \tag{3.23}$$

where

$$x=\left|\frac{\nu^2}{\nu^2-4\Delta^2}\right|^{1/2}\left[1+\left[\frac{\Delta}{\hbar\omega_c}\right]^2\right]^{-1/2} . \tag{3.24}$$

Equations (3.20) and (3.21) give a weak, rather featureless contribution to $\Pi_0(\nu)$. However, $\Pi_0^g(\nu)$ diverges for $\nu=2\Delta$; within this approximation this automatically leads to a δ function in the phonon spectral weight at a frequency just below the superconducting gap 2Δ. This is the result obtained by Balseiro and Falicov,[18] who used the Hamiltonian (3.21) with $g^{(\Delta)}=0$, neglecting vertex corrections

Vertex corrections make a dramatic modification to these results as we should expect from our discussion in Sec. II. We concentrate first on the τ_3 vertex, and calculate Γ from (2.18) with the inclusion of the Coulomb corrections (2.51). In the long-wavelength limit Eq. (2.51) gives the dominant term in the vertex equation owing to the $1/q^2$ behavior of $V_c(q)$ and we obtain

$$\Gamma(\vec{q},\nu)=g^{(\rho)}\tau_3\Big/\left[1+iV_c(q)\int \mathrm{Tr}[\tau_3G(k+q)\tau_3G(k)]\frac{d^4k}{(2\pi)^4}\right] , \tag{3.25}$$

and from (3.15),

$$\Pi^{(\rho)}(\vec{q},\nu)=\Pi_0^{(\rho)}(\vec{q},\nu)/[1-(V_c(q)/g^{(\rho)^2})\Pi_0^\rho(\vec{q},\nu)] . \tag{3.26}$$

Thus the singularity of $\Pi_0^\sigma(q,\nu)$ for $\nu\to 2\Delta$ and $q\to 0$ disappears in the screened version, and we obtain

$$\Pi^\rho(\vec{q},2\Delta)\simeq-\frac{g^{(\rho)^2}}{(4\pi e^2/q^2)} , \tag{3.27}$$

which is small. We note that the denominator of Eq. (3.25) is just the random-phase-approximation dielectric function $\epsilon(\vec{q},\nu)$. Both the vertex Γ and the polarizability Π will diverge when $\epsilon(\vec{q},\nu)\to 0$, which occurs only at the plasma frequency ω_{pl} in either a superconducting or a normal metal. Since $\omega_{\mathrm{pl}}\gg\omega_0$, this has no effect on the phonon self-energy. This is physically reasonable since the electron-phonon coupling term $H_{e\text{-ph}}^\rho$ excites particle-hole pairs near $q\simeq 0$, which are screened by the Coulomb interaction, leading to effects only close to the plasma frequency of the electron system.

We now turn to the renormalization of the τ_1 vertex. As we remarked in Sec. II, the Coulomb renormalization of the τ_1 vertex by Eq. (2.51) is zero, so we can work with Eq. (2.18). We set $\gamma=g^{(\Delta)}\tau_1$, and multiply (2.18) by τ_1 and take the trace, to give

$$\Gamma=g^{(\Delta)}\tau_1\Big/\left[1-\frac{V}{2}\int \mathrm{Tr}[\tau_1G(k+q)\tau_1G(k)]\times\frac{d^4k}{(2\pi)^4}\right] , \tag{3.28}$$

and from (3.18),

$$\Gamma(\nu)=g^{(\Delta)}\tau_1/[1+(V/2g^{(\Delta)^2})\Pi_0^\Delta(\nu)] , \tag{3.29}$$

leading to an expression for the phonon self-energy,

$$\Pi^\Delta(\nu)=\Pi_0^\Delta(\nu)/[1+(V/2g^{(\Delta)^2})\Pi_0^\Delta(\nu)] . \tag{3.30}$$

Note that for $\nu=>2\Delta$, we have

$$\pi_0^\Delta(2\Delta)=-2g^{(\Delta)^2}/V , \tag{3.31}$$

and so the denominators of both (3.29) and (3.30) become zero, leading to singularities in both Γ and Π. This is of course the signature of the τ_1 collective mode with a dispersion relation given by (2.32).

We now find a pole in the phonon spectral weight, at a frequency just below 2Δ given by the solution of (3.14) and (3.30), viz,

$$\nu_g^2=\omega_0^2+2\omega_0\Pi(\nu_g) . \tag{3.32}$$

In terms of the dimensionless coupling constant α, we have for $\alpha\ll 1$,

$$\nu_g^2=\omega_0^2\left[1-\frac{2\alpha}{\pi}(1-\nu_g^2/4\Delta^2)^{-1/2}\right] , \tag{3.33}$$

which has the approximate solution, for $\alpha\ll 1$,

$$\nu_g=2\Delta\left[1-\frac{2\alpha^2}{\pi^2}\left[1-\frac{4\Delta^2}{\omega_0^2}\right]^{-2}\right] . \tag{3.34}$$

The spectral weight $S(\nu)=-1/\pi\,\mathrm{Im}D(\nu)$ is for $\nu<2\Delta$,

$$S(\nu)=\delta(\nu-\nu_g)\frac{8\alpha^2}{\pi^2}\frac{(2\Delta/\omega_0)}{(1-4\Delta^2/\omega_0^2)^3} , \tag{3.35}$$

while for $\nu>2\Delta$ we find a broadened peak close to the bare phonon frequency ω_0 (see Fig. 6).

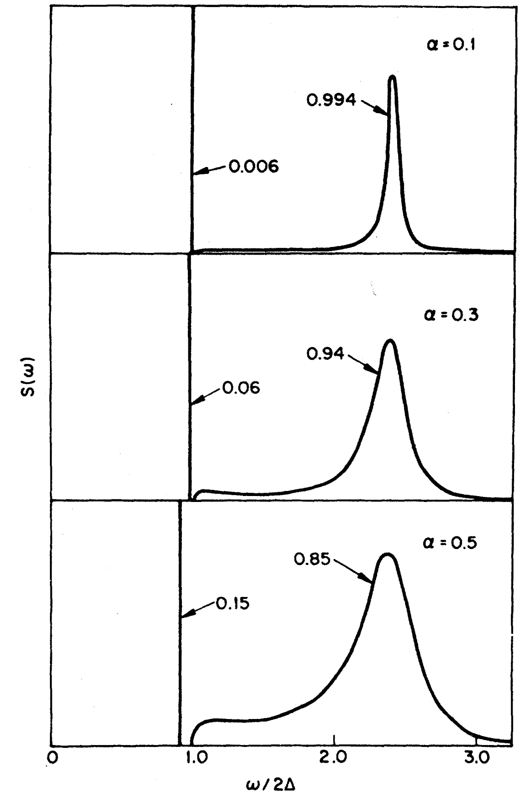

FIG. 6. Phonon spectral weight of the CDW amplitude mode for three different values of the coupling constant α, for $\omega_0=4.8\Delta_0$.

Since α varies with the phonon frequency as ω_0^{-2} from (3.5) and (3.8), the strength of the pole at ν_g varies like ω_0^{-5}; consequently $\omega_0/2\Delta$ must not be too large or the effect will be unobservable.

In Fig. 6 we present the spectral weight, calculated numerically using Eq. (3.30) for α varying from 0.1 to 0.5 with $\omega_0=4.8\Delta_0$ as is appropriate for $NbSe_2$. The phonon in the normal state is assumed undamped. The theory states that below the superconducting transition the peak at ω_0 broadens and a sharp peak appears just below $2\Delta_0$.

C. Experiments in $NbSe_2$

$2H$-$NbSe_2$ is a good candidate in which to observe this new mode. Here we have $\omega_0 \simeq 40$ cm^{-1} and $2\Delta \simeq 17$ cm^{-1}, and we have already shown that the coupling constant α is quite large. Phonon Raman scattering measurements have already been made on $2H$-$NbSe_2$ by SK.[3] They showed that in CDW samples, the CDW amplitude mode (CDW-AM) can be seen in both A and E symmetries close to 40 cm^{-1}. On cooling below $T_c=7.2$ K, they found new "gap" modes in both symmetries at frequencies close to 2Δ. Neither the gap modes nor the the CDW-AM seen in superconducting samples of $2H$-$NbSe_2$ with sufficient impurities seem to suppress the CDW transition. Where both sets of modes are seen, spectral weight is transferred from the gap modes to the CDW-AM when a magnetic field is applied, demonstrating that the gap modes are a coupled excitation of the CDW-AM and superconductivity.

Our theory is in good agreement with the above results; we identify the pole at $\nu=\nu_g$ with the gap modes of SK. To obtain SK's result that $10-15\,\%$ of the phonon spectral weight is transferred into the new gap modes, we need $\alpha \approx 0.4$, which is roughly the value we estimated earlier for the coupling constant in $2H$-$NbSe_2$.

Especially noteworthy in the experiments[3] is the fact that the phonon peak near ω_0 broadens below the superconducting transition and the new feature near $2\Delta_0$ is actually much sharper than the one near ω_0. As discussed above this behavior is reproduced by the theory.

SK observe that as a function of a magnetic field, the strength of the peak near $\omega=2\Delta$ decreases and that in the main phonon peak increases; the positions of the peaks do not change if fields are considerably below H_{c2}. This is precisely the behavior one would expect in a type-II superconductor, where the field increasing above H_{c1}, the density of vortices increases. The volume of the "normal" region (core of vortices) thereby increases, but the magnitude of the gap in the superconducting regions remains almost the same. The strength of the peak near $\omega=2\Delta$ then reflects the volume of the "superconducting region."

$NbSe_2$ was an especially favorable case for observing the amplitude mode since ω_0 is not too far above Δ_0. Other places where it ought to be looked for by Raman scattering are $2H$-TaS_2 and the $A15$ compounds, where both the right optic phonon and superconductivity exist. Direct propagation or resonance experiments to observe the amplitude mode appear to be difficult because of the vanishing group velocity as $q \rightarrow 0$ and the relatively high frequency of the mode and due to the fact that electromagnetic radiation is not a suitable coupling to the modes.

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