Electron-Phonon Interaction and Raman Linewidth in
Superconducting Fullerides.

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Abstract

We propose a microscopic theory of interaction of long wave molecular phonons with electrons in fullerides in the presence of disorder. Phonon relaxation rate and frequency renormalization are discussed. Finite electronic bandwidth reduces phonon relaxation rate at $q = 0$. Electron-phonon coupling constants with molecular modes in fullerides are estimated. The results are in good agreement with photoemission experiments.

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I. INTRODUCTION.

Superconducting fullerides are a new type of materials, where the electronic bandwidth is of the same order as the frequencies of intramolecular modes. [1,2]. Nonadiabaticity of electrons measured by the ratio of characteristic phonon frequency $\omega$ to the Fermi energy $E_F$ is not small. The phonon frequencies are high $\omega \leq 0.2 \, \text{eV}$ and bare Fermi energy is low $E_F \leq 0.2 \, \text{eV}$ [1].

In the past years several different calculations of the electron-phonon coupling constants have been reported for fullerides [3,4]. Some of them yield the strongest coupling with the high frequency $H_g$ modes with a moderate electron-phonon coupling, $\lambda \leq 0.5$. on the other hand picket et al [3] predicted the strongest coupling with the high frequency $A_g(2)$ mode and $\lambda \sim 3$. Similar conclusion has been reached in Ref. [8]. The difference in calculated coupling
constants is quite remarkable, and may result in a qualitatively different understanding of the nature of superconductivity of fullerides. Therefore, the experimental determination of $\lambda$ is required [9–12].

Recently Raman spectra for metallic fullerides at low temperature has been reported in Ref. [9,10]. The linewidth have been analyzed using Allen’s formula for the decay rate of the phonon into electron-hole pair $\gamma$ averaged over all phonon momenta [13]:

$$\bar{\gamma} = \frac{\pi N(0)\lambda\omega^2}{2\kappa},$$  \hspace{1cm} (1)

$N(0)$ is the density of states on the Fermi level, $\lambda$ is electron-phonon coupling constant, $\kappa$ is degeneracy of the phonon mode.

It is well known that the phonon lifetime is determined by the parameter $qv_F/\omega$, $v_F$ is Fermi velocity, and $\omega$ is the frequency of optical phonon. It means that Allen’s formula for the phonon linewidth does not work for optical phonons in $q \approx 0$ limit. In the clean single-band system it is not possible for any optical $q \approx 0$ phonon to decay into electronic excitations because of the conservation of the momentum and the energy. $\Im \Pi(q, \omega) = 0$ for $qv_F \ll \omega$ [14,15]. This result is based on the Ward identity and is independent on vertex corrections (Eqs. (4.20) and (4.21) of the Ref. [14]). Moreover high frequency phonon can not decay into electron-hole pairs if $\omega \geq w$, $w$ is electronic half bandwidth.

It should be pointed out some special comments concerning the pentagonal pinch $A_g(2)$ mode. It shows only a little broadening with doping. The authors in Refs. [9–11] conclude that it is the manifestation of the weak coupling with this mode. As it has been mentioned by Gelfand [2] a $q = 0$ $A_g$ mode shifts all the energy levels on all molecules in the solid by the same amount, and therefore leads to only diagonal elements between band states for the deformation potential. The $q = 0$ $A_g$ modes are thus uncappable of decaying into an electron-hole pair, no matter how strong the electron-phonon coupling is.

Thus, because Fermi velocity $v_F$ is small and the frequency of intramolecular modes are high, the ratio $v_F/\omega$ is small and formula for the phonon lifetime in adiabatic limit $\omega \rightarrow 0$ does not work. The finite contribution to the phonon lifetime for $\omega \rightarrow 0$ appears due to
impurity scattering and orientational disorder \[16\] and the violation of the conservation of the momentum.

In this paper we analyze the phonon relaxation rate and the renormalization of the phonon frequency for \(q = 0\) due to electron-phonon interaction in the presence of disorder and taking into account finite electronic bandwidth. We take into account the effect of disorder in terms of relaxation time \(\tau\) and adopt Fermi-liquid description \(E_F \tau \gg 1\).

II. EFFECT OF DISORDER.

We describe electron-phonon interaction in fullerides by the standard hamiltonian \[17\]. It describes the interaction of \(t_{1u}\) electrons with \(A_g\) and \(H_g\) intramolecular modes:

\[
H = \sum_{k,\sigma,i} \epsilon_k c_{k,\sigma,i}^\dagger c_{k,\sigma,i} + \sum_{k,q,\sigma,i} g_{k} c_{k,\sigma,i}^\dagger c_{k+q,\sigma,i} (b_q^\dagger + b_{-q}) + \sum_q \omega b_q^\dagger b_q,
\]

(2)

where the first term is the kinetic energy of the electrons in threefold degenerate \(t_{1u}\) band, \(c_{k,\sigma,i}^\dagger\) is the creation operator of the electron with momentum \(k\), spin \(\sigma\) and orbital index \(i (i = 1, 2, 3)\), \(b_q^\dagger\) is the creation operator of the phonon with momentum \(q\). Here we take into account momentum dependence of the coupling constant explicitly. For intramolecular modes this dependence is weak, but as we discuss later this dependence is responsible for the finite contribution of the electron-phonon coupling to the phonon relaxation rate at \(q = 0\).

Note that the fine structure of \(H_g\) phonons is usually neglected for the analysis of the relaxation rate with Allen’s formula \[19\]. We also neglect strong degeneracy of \(H_g\) modes. This assumption is quite reasonable if electronic relaxation time is large \(\omega \tau \gg 1\) and if crystal field effects are strong and split of the fivefold degenerate modes is strong \[10\]. It is clear because the nodiagonal elements of the electronic Green’s function appear only due to impurity scattering and are small if \(\omega \tau \gg 1\). It is important, that the interaction constant with single \(H_g\) submode is strongly momentum dependent.

Phonon relaxation rate and frequency renormalization are determined by the real and imaginary parts of the polarization :
\[ \Pi(q = 0, \omega) = i \int \Gamma(k, \omega' + \omega/2, \omega' - \omega/2)g_kG(k, \omega' + \omega/2)G(k, \omega' - \omega/2) \frac{d^3kd\omega}{(2\pi)^4} \quad (3) \]

The equation for the vertex has the form [18] (Fig.1):

\[ \Gamma(k, \omega' + \omega/2, \omega' - \omega/2) = g_k + n_{im}/(2\pi)^3 \int |u(p - k)|^2 G(p, \omega' + \omega/2) \]
\[ G(p, \omega' - \omega/2)\Gamma(p, \omega' + \omega/2, \omega' - \omega/2)d^3p \quad (4) \]

where \( u(p - k) \) is the potential of the single impurity, \( G(k, \omega) = 1/(\omega - \xi - \Sigma(\omega)) \) is electronic Green function, averaged over impurity [18], \( \Sigma(\omega) \simeq -i \frac{\omega^2}{2|\omega|^\tau} \), \( \tau \) is electronic relaxation time, \( n_{im} \) is concentration of impurities.

We define the function:

\[ P(k, \omega' + \omega/2, \omega' - \omega/2) = \Gamma(k, \omega' + \omega/2, \omega' - \omega/2)G(k, \omega' + \omega/2)G(k, \omega' - \omega/2). \quad (5) \]

This function satisfies the equation:

\[ P(k, \omega' + \omega/2, \omega' - \omega/2) = G(k, \omega' + \omega/2)G(k, \omega' - \omega/2)(g_k + \]
\[ n_{im}/(2\pi)^3 \int |u(p - k)|^2 P(p, \omega' + \omega/2, \omega' - \omega/2)d^3p) \quad (6) \]

Main contribution to the integrals appears from the momenta near the Fermi surface \( k \sim k_F \) and we can expand \( g_k \) and \( |u(k-p)|^2 \) in spherical harmonics \( \phi_L(k) \) on the Fermi surface [19]:

\[ g_k = \sum_L g_L\phi_L(k) \quad (7) \]
\[ |u(k-p)|^2 = \sum_{L,L'}\phi_L(k)\Gamma_{L,L'}\phi_{L'}(p)^* \quad (8) \]

For the sake of simplicity we suppose that \( \Gamma_{L,L'} = \delta_{L,L'}\Gamma_L \). The equations for the relaxation times have the form \( 1/\tau = 2\pi N(0)n_{im}\Gamma_0 \), \( 1/\tau_L = 2\pi N(0)n_{im}\Gamma_L \), where \( N(0) \) is the density of state on the Fermi level. Note that \( g_{L=0} \gg g_{L \neq 0} \) for \( A_g \) modes. On the other hand for fivefold degenerate \( H_g \) modes we expect strong \( k \) dependence of the coupling constant.

We define the set of functions \( \Lambda_L(\omega', \omega) \):

\[ \sum_L g_L\phi_L(k)\Lambda_L(\omega', \omega) = n_{im}/(2\pi)^3 \int |u(k-p')|^2 P(p', \omega' + \omega/2, \omega' - \omega/2)d^3p, \quad (9) \]
and derive the equation for $\Lambda_L(\omega',\omega)$:

$$
\sum_L g_L \phi_L(l) \Lambda_L(\omega',\omega) = \frac{n_{im}}{(2\pi)^3} \sum_M (1 + \Lambda_M(\omega',\omega)) \int |u(k-p)|^2 g_M \phi_M(p) G(p,\omega'/2) G(p,\omega'/2) d^3p. 
$$

Integrating out the angles in Eq.(10) and taking into account Eq.(8) we obtain:

$$
\Lambda_L(\omega',\omega) = \begin{cases} 
1/\tau_L & |\omega'| < |\omega| \\
0 & |\omega'| > |\omega| 
\end{cases}
$$

where $1/\tau^*_L = 1/\tau - 1/\tau_L$

Note that for $L = 0$ $\Lambda_0(\omega',\omega) = i/\tau \omega$. The largest term in the expansion of the coupling constant $g_0$ does not contribute to the $q = 0$ phonon relaxation rate. Substituting Eq.(5) to Eq.(3) and taking into account Eqs.(9),(6) and (11) we obtain:

$$
\Pi(0,\omega) = -2i \sum_{L\neq 0} g_L^2 N(0)/\tau^*_L. 
$$

Here we take into account that $\int d\omega' (\Sigma(\omega + \omega'/2) - \Sigma(\omega - \omega'/2)) = 0$.

As a result we obtain the formula for the phonon relaxation rate $\gamma(\omega)$:

$$
\gamma(\omega) = -3\Pi(0,\omega) = 2 \sum_{L\neq 0} \frac{g_L^2 N(0) \omega \tau^*_L}{\omega^2 \tau^*_L + 1} 
$$

It follows from the Eq.(13) phonon relaxation rate at $q \to 0$ is determined by the parameter $<g_k^2> - <g_k>^2$, where $<..>$ is average over Fermi surface. This formula is strongly different from Allen’s formula \[13\]. (i) Phonon relaxation rate is proportional to the averaged over Fermi surface $k$-dependent component of the electron-phonon coupling constant. Phonon relaxation rate due to electron-phonon coupling is equal to zero if coupling constant is independent of the electronic momentum $k$. (ii) Phonon relaxation rate is proportional to the impurity scattering relaxation rate of electrons at low temperatures $1/\tau^*$. Therefore, momentum dependence of the electron-phonon interaction is responsible for the finite Raman linewidth.
It should be pointed out, that similar formula for the relaxation rate of the optical phonons in metals was derived from kinetic equation in Ref. [20] and Green’s function technique [21]. Note that formula (13) is different from that derived in Ref. [20]. New term proportional to \( \Lambda(\omega', \omega) \) appears in the equation for \( \Pi(\omega) \) due to correct average of the vertex over impurities. Neglecting this term one can derive the same formula for relaxation rate as Eq.(18) of Ref. [20].

Extensive numerical calculations of the phonon lifetime, using spherically symmetrical coupling have been performed in Ref. [22]. It has been shown that diagonal component of the polarization is site dependent in disordered phase. This fact is in agreement with formula (13). Because \( H_g \) modes are not spherically symmetrical the interaction with the five split submodes will have large \( L \neq 0 \) harmonics on the Fermi surface even in the case of spherically symmetrical bare interaction.

III. BANDWIDTH EFFECT.

In superconducting fullerides there are a number of molecular modes with the frequencies of the order of bare bandwidths. These are pentagonal pinch mode \( A_g(2) \) \( \omega \approx 1500cm^{-1} \) and four \( H_g \) modes with \( \omega \approx 1200 – 1600cm^{-1} \). Because of conservation of energy these modes cannot decay into electron-hole pair in the clean system. Note that in the limit of \( w \ll \omega \) phonon relaxation rate is equal to 0 in the lowest order in coupling constant.

We use Eqs. (3) and (4) for the polarization and lorenzian form of the density of states to take into account the finite bandwidth:

\[
N(\xi) = \frac{2\nu}{\pi} \frac{w}{\xi^2 + w^2} \tag{14}
\]

where \( w \) is effective half bandwidth, \( \nu \) is orbital degeneracy. For the \( t_{1u} \) band \( \nu = 3 \). Using Eq.(14) we can derive the equation for electronic self-energy averaged over impurities in ladder approximation [23]:

\[
\Sigma(\omega) = x w^2 \frac{1}{\omega + i w / |\omega|} - \Sigma(\omega) \tag{15}
\]
where \( x = \nu \Gamma_0 n_{im}/w^2 = 1/2\tau w \) is dimensionless concentration of impurities.

Integrating out the angle in Eq. (10) and taking into account Eq. (8) we obtain the formula for \( \Lambda_L(\omega', \omega) \):

\[
\Lambda_L(\omega', \omega) = x_L \frac{\Sigma(\omega - \omega'/2) - \Sigma(\omega + \omega'/2)}{\omega + \frac{x_L}{x}(\Sigma(\omega - \omega'/2) - \Sigma(\omega + \omega'/2))}
\]

where \( x_L = \nu \Gamma_L n_{im}/w^2 = 1/2\tau_L w \). We have used here integral equation for the electronic self-energy in ladder approximation [18, 23]. Note, that Eq. (16) is equivalent to the Eq. (11) if \( \Sigma(\omega) = -i\omega/|\omega|\tau \).

Equation for the \( L \) component of the polarization has the form:

\[
\Pi_L(\omega) = -\frac{2i g^2 L \nu}{\pi x w} \int dy \frac{\Sigma(y - \omega/2) - \Sigma(y + \omega/2)}{\omega + \frac{x_L}{x}(\Sigma(y - \omega/2) - \Sigma(y + \omega/2))}
\]

Taking into account that \( E_F \tau \simeq w \tau \gg 1 \) we obtain:

\[
\Sigma(\omega) = x w^2 \frac{1}{\omega + i\omega/|\omega|}
\]

Substituting Eq. (18) into Eq. (17) and integrating out \( y \) we derive the formulae for imaginary and real parts of the polarization:

\[
\Re \Pi(\omega) = \sum_L \frac{2g^2 L N(0)}{w(\omega/w)^2 \tau_L^*} \left( \omega \ln (1 + (\omega/w)^2) - 4w \arctan (\omega/w) \right) + 1
\]

\[
\gamma(\omega) = -\Im \Pi(\omega) = \sum_L \frac{4g^2 L N(0)}{w(\omega/w)^3 ((\omega/w)^2 + 4) \tau_L^*} \left( \ln (1 + (\omega/w)^2) + \omega \arctan (\omega/w)/w \right)
\]

Eq. (20) reduces to Eq. (13) in the large bandwidth limit \( \omega/w \ll 1 \). In the opposite limit \( \omega/w \gg 1 \) the relaxation rate is strongly reduced:

\[
\gamma(\omega) = -\Im \Pi(\omega) = \sum_L \frac{2\pi g^2 L N(0) w^3}{\omega^4 \tau_L^*}
\]

**IV. CONCLUSION.**

In conclusion we analyze the experimental data on the Raman scattering in fullreides [9, 10] using the correct formula for \( q = 0 \) phonon relaxation rate. Unfortunately, direct estimate of
the coupling constant is practically impossible. It requires exact form of angular dependence of electron-phonon coupling constant on the Fermi surface and electronic relaxation rate $1/\tau$. However, if we assume that $g^2_L \sim< g^2 > \sim \lambda_\omega/N(0)$ and use the value for $H_g(1)$ mode from the photoemission experiments [11,12], we can calculate coupling constants for another 7 $H_g$ modes using the formula:

$$\gamma_i/\gamma_j \sim \lambda_i/\lambda_j$$\hspace{1cm}(22)$$

If we suppose that $\lambda_1/N(0) \approx 0.02eV$ [11,12] for $H_g(1)$ mode, we obtain the coupling constants $\lambda_i/N(0)$ for other 7 $H_g$ modes (Table 1). Note that Eq.(22) is valid only for $H_g$ modes, because angular dependence of the coupling constant on the Fermi surface for $A_g$ modes is strongly different from that for $H_g$ modes and we do not expect the cancellation of angular factor in Eq.(13). From the Table 1 we can conclude:

- Using Eq.(22) and the experimental Raman linewidths we obtain coupling constants for $H_g$ modes. They are in good agreement with photoemission data. Note that Allen’s formula underestimates the coupling constants by the order of magnitude for the most of the $H_g$ modes.

- The difference in coupling constants for $H_g(2)$ and $H_g(3)$ modes is probably connected with the fact that in the analysis of photoemission spectra of $C_{60}$ the interaction with $A_g(1)$ mode has been neglected [11,12].

- The difference in estimated constants for $H_g(7,8)$ modes is due to frequency dependence of electronic relaxation time $\tau$. Because the interaction with low frequency modes is quite strong we expect strong frequency dependence of $\tau$ and Eq.(22) is not valid.

- Due to high symmetry of $A_g(1,2)$ modes angular dependence of the coupling constants is weak and Eq.(22) does not work.
It should be pointed out that frequency renormalization of these modes is not due to
effects considered in the paper. Indeed, the downshift of $A_g(2)$ mode is about $6\text{ cm}^{-1}$ per
elementary charge on the $C_{60}$. If we suppose that this downshift is due to interaction of
phonons with band electrons one should expect the maximum of downshift near the half-
filled band ($x = 3$) and the absence of the downshift for $x = 6$. In an isolated molecule there
is also a frequency renormalization when molecule becomes charged. Theoretical estimates
of the frequency shift due to the charging of $C_{60}$ molecule are in a reasonable agreement
with experiments [24].

We have estimated coupling constants of the conducting electrons with the molecular
phonons in superconducting fullerides from Raman experiments. The results are in good
agreement with that obtained from photoemission measurements. Note that these constants
with proper account of polaron effect lead to correct values of $T_c$, isotope effect and pressure
dependence of $T_c(P)$ [12].

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TABLE I. Coupling constants obtained from Raman measurements using Allen’s formula (AF), Eq.(13) and from photoemission experiments (PES).

| H   | \(\omega\) (cm\(^{-1}\)) | \(\gamma\) (cm\(^{-1}\)) | \(\lambda/N(0)\) (eV) AF [10] | \(\lambda/N(0)\) (eV) Eq.(13) | \(\lambda/N(0)\) (eV) PES [11] | \(\lambda/N(0)\) (eV) PES [12] |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| H(1) | 270             | 20              | 0.048           | 0.020           | 0.019           | 0.020           |
| H(2) | 432             | 21              | 0.020           | 0.021           | 0.040           | 0.038           |
| H(3) | 709             | 8               | 0.002           | 0.008           | 0.013           | 0.019           |
| H(4) | 773             | 10              | 0.003           | 0.010           | 0.018           | 0.018           |
| H(5) | 1100            | 11              | 0.001           | 0.011           | 0.012           | 0.009           |
| H(6) | 1248            | 10              | 0.001           | 0.010           | 0.005           | 0.001           |
| H(7) | 1425            | 46              | 0.004           | 0.046           | 0.017           | 0.000           |
| H(8) | 1572            | 42              | 0.003           | 0.042           | 0.023           | 0.000           |
FIGURES

FIG. 1. Equation for the vertex function $\Gamma(k, \omega'+\omega/2, \omega'-\omega/2)$
FIGURES

FIG. 1. V.I. Aksenov, V.V. Kabanov

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