Phonon anomalies due to strong electronic correlations in layered organic metals

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We show how the coupling between the phonons and electrons in a strongly correlated metal can result in phonon frequencies which have a non-monotonic temperature dependence. Dynamical mean-field theory is used to study the Hubbard-Holstein model that describes the $\kappa$-(BEDT-TTF)$_2$X family of superconducting molecular crystals. The crossover with increasing temperature from a Fermi liquid to a bad metal produces phonon anomalies that are consistent with recent Raman scattering and acoustic experiments.

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An important problem concerning strongly correlated metals such as heavy fermions, cuprates and organic superconductors is understanding the interplay of the strong interactions between electrons and the interactions between the electrons and phonons. This is particularly relevant to understanding the question of whether the phonons play any role in superconductivity [1]. In this Letter we show how strong electronic correlations can lead to phonon frequencies varying with temperature. Although, our calculations focus on explaining recent experiments on a particular family of organic superconductors, the physics involved is relevant to other strongly correlated metals in which there is a significant redistribution of the electronic spectral weight as the temperature is varied.

The quasi-two-dimensional organic superconductors, $\kappa$-(BEDT-TTF)$_2$X, are strongly correlated electron systems [2,3]. Recent Raman scattering experiments [5] find that in the metallic state the frequency of certain phonons associated with the BEDT-TTF molecules have a non-monotonic temperature dependence below 200 K. Acoustic experiments [6] find that around 40 K there is a significant softening of the speed of longitudinal sound propagating perpendicular to the layers. This softening, of the order of a few per cent, is more than an order of magnitude larger than the softening associated with the superconducting transition. We will show that such a temperature dependence can arise due to the destruction of Fermi liquid quasiparticles that occurs above the coherence temperature, $T^*$ [6,11]. Anomalies in acoustic phonons in the heavy fermion UPt$_3$ have also been seen at temperatures of the order of $T^*$ [11].

The simplest possible strongly correlated electron model for the $\kappa$-(BEDT-TTF)$_2$X family is a single band Hubbard model on an anisotropic triangular lattice at half-filling [14]. We have found [7] that many of the transport properties of the metallic phase are consistent with the predictions of dynamical mean-field theory (DMFT) [8] which captures exactly the dynamical fluctuations at each lattice site, but neglects all non-local spatial correlations. In order to understand the effect of electronic correlations on the molecular phonon modes we have considered the relevant Holstein-Hubbard model where the phonon amplitude couples linearly to the local charge density. The phonon self-energy is proportional to the electronic density-density correlation function which we calculate using DMFT. When the electron-electron interactions are sufficiently large we find that phonon frequencies can have a non-monotonic temperature dependence. This is related to the crossover from a Fermi liquid to a bad metal that occurs with Increasing temperature and has a significant effect on the electronic transport properties [9]. The actual form of the temperature dependence of the shift in phonon frequency varies significantly with the phonon frequency.

We consider the Hubbard-Holstein Hamiltonian

$$H = t_1 \sum_{ij,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + t_2 \sum_{ik,\sigma} (c_{i\sigma}^\dagger c_{k\sigma} + \text{h.c.})$$

$$+ U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i\sigma} n_{i\sigma}$$

$$+ \frac{g}{\sqrt{2}} \sum_{i\sigma} (a_i^{\dagger} + a_i) n_{i\sigma} + \omega_0 \sum_i a_i^{\dagger} a_i$$

where the electronic part describes electrons on the antibonding orbitals of each dimer of BEDT-TTF molecules which are located on an anisotropic triangular lattice. $t_1$ and $t_2$ are the nearest and next-nearest-neighbour hoppings. $U$ is the Coulomb repulsion on a triangular lattice. $t_1$ and $t_2$ are the nearest and next-nearest-neighbour hoppings. $U$ is the Coulomb potential. The operator, $c_i^\dagger$, creates an electron on the anti-bonding orbital of the dimer. The operator, $a_i^\dagger$, creates a phonon at site $i$, which describes a molecular vibration of frequency $\omega_0$. We consider only the in-phase vibrations of the two phonon modes associated with the dimer; these can be activated by Raman scattering (see below). $g$ is the coupling between the Raman active phonon and the electron density on a dimer.

We focus on the parameter regime where the electron-electron interaction is dominant and we are well away from any instability (superconducting or charge-density-wave) due to the electron-phonon coupling. We can then decouple the set of Dyson’s equations in the electron-
phonon problem, so that the electron self-energy contains the electron-electron scattering mechanism only; any effects coming from the interaction of the electrons with phonons on the electron propagator are neglected. The electron Green’s function is given by [9]

\[ G_\sigma(k, i\omega_n) = \frac{1}{i\omega_n - \epsilon_k - \Sigma(i\omega_n)} \]  

(2)

where \( \omega_n = (2n+1)\pi T \) is a Matsubara fermion frequency for temperature \( T \). \( \epsilon_k = t_1 \cos(k_x) + t_2 \cos(k_x + k_y) \) is the dispersion relation for the anisotropic triangular lattice. \( \Sigma(i\omega_n) \) is the momentum independent self-energy computed within DMFT from the associated Anderson impurity problem, using the iterative perturbation theory. Details can be found elsewhere [10].

The phonon problem is solved separately through the associated Dyson equation

\[ D(q, \omega) = \frac{\omega_q^2}{\omega^2 - \omega_q^2 - \frac{g^2}{g^0} \Pi(q, \omega)/2} \]  

(3)

where \( \Pi(q, \omega) \) is the electronic density-density correlation function (or polarization) which includes the full effect of the electron-electron interactions at the level of DMFT. For \( \Pi(q, \omega) \) we take the particle-hole bubble, which, in terms of Matsubara frequencies is given by

\[ \Pi(q, i\nu_n) = T \sum_{k, \sigma, \omega_n} G_\sigma(k, i\omega_n) G_\sigma(k + q, i\omega_n + i\nu_n) \]  

(4)

and \( G_\sigma(k, i\omega_n) \) is the Green’s function of the electrons obtained from the solution of (3). The temperature dependence of the polarization predominantly comes from the temperature dependence of the individual one-electron Greens functions. Fig. [11] shows how the Fermi liquid quasiparticle peak in the spectral density of states is strongly temperature dependent. We show results for the case, \( t_1 = t_2 = t \) [12], which corresponds to a triangular lattice.

Due to the electron-phonon interactions, the phonon frequency is shifted from its bare value \( \omega_0 \) and has a finite lifetime. This shift can be obtained from the poles of (3), which we denote by \( \tilde{\omega}_q = \omega_q + i\Gamma_q \). For weak electron-phonon coupling the frequency shift is

\[ \frac{\Delta \omega}{\omega_0} = \frac{\omega_q - \omega_0}{\omega_0} = \frac{g^2}{4} \Pi^R(q, \omega_0) \]  

(5)

where \( \Pi^R(q, \omega_0) \) denotes the real part of the polarization. The phonon damping is proportional to the imaginary part of the polarization. Fig. [11] shows the temperature dependence of the real part of the polarization, \( \Pi^R(q = 0, \omega_0) \), for different bare phonon frequencies, \( \omega_q \).

Our DMFT calculations show that for frequencies close to \( U/2 \) and sufficiently strong interactions the phonon frequency can have a non-monotonic temperature dependence near the coherence temperature, \( T^* \). From Fig. [13], we find that \( T^* \approx 0.1t \sim 100K \), for \( t \sim 0.1 \) eV. However, this behaviour disappears gradually as \( U \) decreases and becomes smaller than the bandwidth, \( W = 4.5t \). This is clearly seen for \( U = 2t \). The effective mass enhancement for \( U = 5.5t \) is \( m^*/m \approx 3.8 \); this is in the range of the effective masses found in \( \kappa-(BEDT-TTF)_2X \) [14]. Lin et al. [8] have measured an anomalous softening below about 100 K of the Raman frequency shifts in the phonons, \( \nu_0 = 505 \mathrm{cm}^{-1} \) and \( \nu_0(B3) = 890 \mathrm{cm}^{-1} \) for \( \kappa-(BEDT-TTF)_2 \mathrm{Cu(SCN)}_2 \) (see Fig. 5 in ref. [7]). The higher frequency mode, \( \nu_3 = 1478 \mathrm{cm}^{-1} \), also exhibits a strong (but monotonic) temperature dependence. Table [11] gives the magnitude of the total temperature dependence between about 10 and 300 K. Other phonons do not exhibit such a strong temperature dependence [13].

We find even stronger effects for low-frequency phonons. In Fig. 3 the real part of the phonon self-energy [14] is plotted for \( q = 0 \) and \( \omega_0 = 0.05t \). For strong correlations \( (U > W) \), a dip in the real part of the self-energy appears at the coherence temperature, \( T^* \). For decreasing values of \( U \), the position of the dip moves to higher temperatures (because \( T^* \) increases) and the dip becomes smaller. These results could be relevant to understanding recent acoustic experiments [11]. The velocity of ultrasonic waves which are propagating perpendicular to the layers was found to have a non-monotonic temperature dependence. These waves have frequencies of 100 MHz and velocities of about 2000 cm/s. The velocity versus temperature shows a broad dip of a few per cent around 40 K. This softening becomes larger as the pressure is decreased and is about three times larger for \( \kappa-(BEDT-TTF)_2 \mathrm{Cu[N(CN)]}_2 \mathrm{Br} \) than \( \kappa-(BEDT-TTF)_2 \mathrm{Cu[SCN]}_2 \). Decreasing the pressure or changing the anion from \( \mathrm{Cu}[N(SCN)]_2 \) to \( \mathrm{Cu}[N(CN)]_2 \) Br corresponds to increasing the electronic correlations or increasing of \( U/t \). For example, it has been observed that as the pressure decreases \( m^*/m_c \) increases and the metal-insulator transition is approached [13-14]. Our calculated variation of the position of the dip with \( U \) is in qualitative agreement with the observed variation of the position of the dip with pressure (compare Fig. 4 in Ref. [3]). However, caution is in order because further experiments [11-13] find that the softening only occurs for waves propagating parallel to the layers when their polarisation is perpendicular to the layers. Our model can only
explain this if modulation of the interlayer spacing has a much stronger coupling to the electronic charge density within the dimers than modulation of the interdimer spacing.

The family $\kappa$-(BEDT-TTF)$_2X$ are particularly amenable to study the effect of electronic correlations on the molecular phonons because the dimer structure of the molecular crystal allows us to extract the electron-phonon coupling strength $g$ from experimental data. The crystal structure is such that the BEDT-TTF molecules are arranged in pairs that are reasonably well separated from one another. There are three electrons per dimer. For each phonon mode on a molecule there is a symmetric and an anti-symmetric combination on the dimer. By parity conservation, the anti-symmetric modes are infra-red active and the symmetric modes are Raman active. If there is a Holstein model coupling for a single molecule the Hamiltonian for a dimer is [16]

$$H_{ep} = -t_0 \left( c_1^{\dagger} c_2 + c_2^{\dagger} c_1 \right) + \sum_{i=1}^{2} g c_i^{\dagger} c_i \left( a_i + a_i^{\dagger} \right) + \omega_0 a_i^{\dagger} a_i$$

where $t_0$ is the transfer integral for hopping between molecules within the dimer. This is much larger than the hoppings $t_1$ and $t_2$ between dimers that appears in [1] [4]. The bonding and anti-bonding orbitals associated with the dimer are separated by $2t_0$, even in the presence of a Hubbard term. The Hamiltonian can be re-written as

$$H_{ep} = -t_0 \left( c_1^{\dagger} c_2 + c_2^{\dagger} c_1 \right) + \sum_{\alpha=\pm} \frac{g}{\sqrt{2}} n_{\alpha} \left( a_{\alpha} + a_{\alpha}^{\dagger} \right) + \omega_0 a_{\alpha}^{\dagger} a_{\alpha}$$

where $a_{\pm} = \frac{1}{\sqrt{2}} \left( a_1 \pm a_2 \right)$ and $n_{\pm} = c_1^{\dagger} c_1 \pm c_2^{\dagger} c_2$. The $n_{\pm}$ term is the same as the number operator, $n_i$, appearing in [9]. It is the fluctuations in this term that produce the temperature dependence shown in Figures 2 and 3. In contrast, the infrared active mode will not couple to these fluctuations and so should have no such temperature dependence.

If the number of electrons on the dimer is fixed then the symmetric mode has frequency $\omega_0$. A second-order perturbative calculation [16] predicts that for $\omega_0 \ll t_0$, the infra-red frequency $\omega_{IR}$ will be smaller than the Raman frequency ($\omega_R = \omega_0$),

$$\frac{\omega_{IR} - \omega_R}{\omega_R} = -\frac{g^2}{2\omega_0 t_0}.$$  \hspace{1cm} (6)

Table I lists the details of the measured frequency shifts for three different modes for $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$. For $t_0 = 0.3$ eV [17] these values are used together with [18] to evaluate the electron-phonon coupling $g$. The values obtained are in reasonable agreement with those found in a MNDO frozen phonon quantum chemistry calculation [13] on a single BEDT-TTF molecule.

Zeyher and Zwicknagl [12] considered the frequency shift of phonons when they enter the superconducting phase. Within the framework of BCS theory, phonons with frequency $\omega_0$ much smaller than the Fermi energy and much larger than the superconducting gap $\Delta$ will harden by an amount

$$\frac{\omega_{IR} - \omega_R}{\omega_0} = \frac{8g^2 N(0)}{\omega_0} \left( \frac{\Delta}{\omega_0} \right)^2 \ln \left( \frac{\omega_0}{\Delta} \right)$$  \hspace{1cm} (7)

where $N(0)$ is the density of states per spin at the Fermi energy. There should be no shift in the frequency of the infra-red active mode on entering the superconducting phase. Using $\Delta \sim 2k_B T_c \sim 0.002$ eV and the values for $g$ in Table I we have evaluated the estimated shift in the phonon frequency for three different modes in Table II. Eldridge et al. [3] found that in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br the $\nu_{g0}(B_3g)$ mode at 890 cm$^{-1}$ hardened by about 0.2 % on entering the superconducting phase. A shift in this mode was not detected in $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$. No frequency shift in the other high-frequency modes was detected to within about 0.1 %. However, one should be cautious about making quantitative comparisons between experiment and Table I since (7) is only valid for $\omega_0 \ll t$ and we have $\omega_0 \sim t$.

Pedron et al. did observe the hardening of modes with frequencies ranging from 27 to 134 cm$^{-1}$ [21]. For acoustical phonons the softening will scale like $\left( \omega_0/\Delta \right)^2$ and so be much smaller than the effects shown in Fig. 3.

In conclusion, we have shown how in a strongly correlated metal the redistribution of spectral weight over the scale of the band width with varying temperature can result in phonon frequencies with anomalous temperature dependence. The effects involved are larger than those associated with the superconducting transition because the latter only involves a redistribution of spectral weight over energies of the order of the superconducting gap which is much less than the band width.

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[1] O. Gunnarsson, Rev. Mod. Phys. 69, 575 (1997).
[2] H. Kino and H. Fukuyama, J. Phys. Soc. Jap. 65, 2158 (1996).
[3] K. Kanoda, Physica C 282, 299 (1997).
[4] R. H. McKenzie, Comments Cond. Mat. Phys. 18, 309 (1998).
[5] J. Merino and R. H. McKenzie, Phys. Rev. B 61, 7996 (2000).
[6] J. Merino and R. H. McKenzie, Phys. Rev. B, to appear 15 July (2000).
[7] Y. Lin et al., Phys. Rev. B 58, R599 (1998).
[8] K. Frikach et al., Phys. Rev. B 61, R6491 (2000).
[9] A. Georges et al., Rev. Mod. Phys. 68, 13 (1996).
[10] Th. Pruschke, M. Jarrell, and J. K. Freericks, Adv. Phys. 44, 187 (1995).
[11] V. Müller, et al., Phys. Rev. Lett. 56, 248 (1986); J. Grolle, V. Müller, and K. H. Bennemann, Phys. Rev. B 35, 4493 (1987). Both the temperature dependence of the acoustic attenuation and the thermopower exhibit peaks around 10 K.
[12] Relaxing this condition produces only small quantitative changes in our results.
[13] J. E. Eldridge et al., Phys. Rev. B 57, 597 (1998).
[14] In the calculations shown in Fig. 3 a small imaginary part has been added to the self-energy ($\Sigma I (\omega = 0) = 0.1\epsilon$) to allow for the effect of impurities and to be consistent with the observed resistivity at low temperatures [K. Murata et al., Synth. Met. 27, A623, (1988)].
[15] M. Poirier, private communication.
[16] M. J. Rice, Solid State Commun. 31, 93 (1979). Note, that Rice’s calculations are for two electrons per dimer. For the case of three electrons per dimer considered here the Hubbard $U$ has no effect on the phonon frequency shift.
[17] A. Fortunelli and A. Painelli, J. Chem. Phys. 106, 8051 (1997).
[18] J. Shumway, S. Chattopadhyay and S. Satpathy, Phys. Rev. B 53, 6677 (1996).
[19] R. Zeyher and G. Zwicknagl, Z. Phys. B 78, 175 (1990).
[20] D. Pedron et al., Synth. Met. 85, 1509 (1997).
[21] J. E. Eldridge et al., Spectrochim. Acta A 53, 565 (1997).
TABLE I. Parameters for three molecular phonons in \( \kappa-(BEDT-TTF)_2\text{Cu(SCN)}_2 \). The experimental values are taken from Reference [21]. The difference between the infra-red frequency, \( \omega_{IR} \) and the Raman frequency, \( \omega_R \), and equation (6) is used to estimate (est.) the electron-phonon couplings \( g \). These values are compared with values of \( g \) calculated by a quantum chemistry (QC) calculation [18]. \( \Delta \omega_R(\mathcal{T}) \) is the observed magnitude of the temperature dependence of the Raman-active mode between about 10 K and 300 K. \( \Delta \omega_{SC} \) is an estimate of the increase of the phonon frequency on entering the superconducting phase, based on equation (7).

| Mode | Observed Frequency (cm\(^{-1}\)) | e-p coupling, \( g \) (eV) | \( \frac{\omega_R - \omega_{IR}}{\omega_R} \) (%) | est | QC | \( \frac{\Delta \omega_R(\mathcal{T})}{\omega_R} \) (%) | \( \frac{\Delta \omega_{SC}}{\omega_0} \) (%) |
|------|---------------------------------|-----------------------------|---------------------------------|-----|----|-------------------------------|-------------------------------|
| \( \nu_3 \) | 1276 1478 | 14 0.14 | 0.14 | 0.3 | 0.13 |
| \( \nu_9 \) | 431 505 | 15 0.07 | 0.08 | 1 | 0.7 |
| \( \nu_{60} \) | 881 890 | 1 0.02 | ? | 0.3 | 0.02 |
FIG. 1. Spectral densities of the metallic phase of the Hubbard model at half-filling calculated for the triangular lattice using dynamical-mean field theory. The bare density of states ($U = 0$) is shown as a dotted line. A peak at the Fermi energy due to a coherent band of Fermi liquid quasiparticles and two incoherent Hubbard bands situated at $\omega = \pm U/2$, are clearly resolved when the electron-electron interactions are larger than the metal bandwidth, $W$ ($U \geq W = 4.5t$). The quasiparticle peak is strongly temperature dependent and its spectral weight becomes small as $T > T^*$, $T^*$, being the coherence temperature. This strong temperature dependence of the spectral density is the origin of the temperature dependence of the phonon frequencies discussed in this paper.

FIG. 2. Temperature dependence of the real part of the polarization for different frequencies and correlation strengths. Due to their coupling to electrons the phonons undergo a frequency shift that is proportional to this polarization. Significant temperature dependence occurs when two conditions are simultaneously satisfied: (i) $\omega_0$, is close to $U/2$ and (ii) electron-electron interactions are sufficiently strong that there are well-defined Hubbard bands (compare Fig. 1). For $U/t = 2$ the temperature dependence is negligible, as expected from the slight temperature dependence of the spectral density.

FIG. 3. Temperature dependence of the real part of the polarization for $\omega_0 = 0.05t$ and different values of $U/t$. A dip appears at the coherence temperature, $T^*$, and it becomes more sharply defined as the electron-electron interactions increase. The position of the dip shifts towards lower temperatures as $U/t$ increases.