

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 that have a nonmonotonic temperature dependence. Dynamical mean-field theory is used to study the Hubbard-Holstein model that describes the κ -(BEDT-TTF)₂X [where BEDT-TTF is bis-(ethylenedithia-tetrathiafulvalene)] family of superconducting molecular crystals. The crossover with increasing temperature from a Fermi liquid to a bad metal produces phonon anomalies that are relevant to recent Raman scattering and acoustic experiments.

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 paper, 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, κ -(BEDT-TTF)₂X, are strongly correlated electron systems.²⁻⁶ Recent Raman scattering experiments⁷ find that in the metallic state the frequency of certain phonons associated with the BEDT-TTF molecules has a nonmonotonic temperature dependence below 200 K. Acoustic experiments^{8,9} 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 percent, 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 occur above the coherence temperature, T^* .^{5,10,11} Anomalies in acoustic phonons in the heavy fermion UPt₃ have also been seen at temperatures of the order of T^* .¹²

The simplest possible strongly correlated electron model for the κ -(BEDT-TTF)₂X family is a single-band Hubbard model on an anisotropic triangular lattice at half-filling.^{2,4} We have found⁵ that many of the transport properties of the metallic phase are consistent with the predictions of dynamical mean-field theory (DMFT),¹⁰ which captures exactly the dynamical fluctuations at each lattice site, but neglects all nonlocal 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 inter-

actions are sufficiently large, we find that phonon frequencies can have a nonmonotonic 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.⁵ 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

$$\begin{aligned}
 H = & t_1 \sum_{ij,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + t_2 \sum_{ik,\sigma} (c_{i\sigma}^\dagger c_{k\sigma} + \text{H.c.}) \\
 & + U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i\sigma} n_{i\sigma} + \frac{g}{\sqrt{2}} \sum_{i\sigma} (a_i^\dagger + a_i) n_{i\sigma} \\
 & + \omega_0 \sum_i a_i^\dagger a_i, \tag{1}
 \end{aligned}$$

where the electronic part describes electrons on the antibonding orbitals of each dimer of BEDT-TTF molecules that are located on an anisotropic triangular lattice. t_1 and t_2 are the nearest- and next-nearest-neighbor hoppings. U is the Coulomb repulsion between two electrons on the same site and μ is the chemical potential. The operator c_i^\dagger creates an electron on the antibonding orbital of the dimer. The operator a_i^\dagger creates a phonon at site i , which describes a molecular vibration of frequency ω_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 by¹⁰

$$G_\sigma(\mathbf{k}, i\omega_n) = \frac{1}{i\omega_n - \epsilon_{\mathbf{k}} - \Sigma(i\omega_n)}, \tag{2}$$

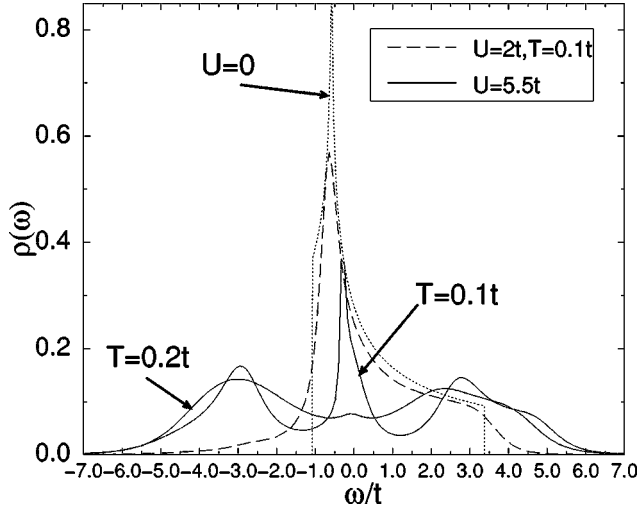


FIG. 1. Spectral densities of the metallic phase of the Hubbard model at half-filling calculated for the triangular lattice using dynamical mean-field theory. The bare density of states ($U=0$) is shown as a dotted line. A peak at the Fermi energy due to a coherent band of Fermi liquid quasiparticles 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.

where $\omega_n = (2n+1)\pi T$ is a Matsubara fermion frequency for temperature T . $\epsilon_{\mathbf{k}} = t_1(\cos(k_x) + \cos(k_y)) + t_2 \cos(k_x + k_y)$ 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.^{10,5}

The phonon problem is solved separately through the associated Dyson equation,

$$D(\mathbf{q}, \omega) = \frac{\omega_0^2}{\omega^2 - \omega_0^2 - g^2 \omega_0^2 \Pi(\mathbf{q}, \omega)/2}, \quad (3)$$

where $\Pi(\mathbf{q}, \omega)$ 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 $\Pi(\mathbf{q}, \omega)$, we take the particle-hole bubble, which, in terms of Matsubara frequencies, is given by

$$\Pi(\mathbf{q}, i\nu_n) = T \sum_{\mathbf{k}, \sigma, \omega_n} G_{\sigma}(\mathbf{k}, i\omega_n) G_{\sigma}(\mathbf{k} + \mathbf{q}, i\omega_n + i\nu_n) \quad (4)$$

and $G_{\sigma}(\mathbf{k}, i\omega_n)$ is the Green's function of the electrons obtained from the solution of Eq. (2). The temperature dependence of the polarization predominantly comes from the temperature dependence of the individual one-electron Green's functions. Figure 1 shows how the Fermi liquid quasiparticle peak in the spectral density of states is strongly temperature dependent. We show results for the case $t_1 = t_2 = t$, which corresponds to a triangular lattice.¹³

Due to the electron-phonon interactions, the phonon frequency is shifted from its bare value ω_0 and has a finite

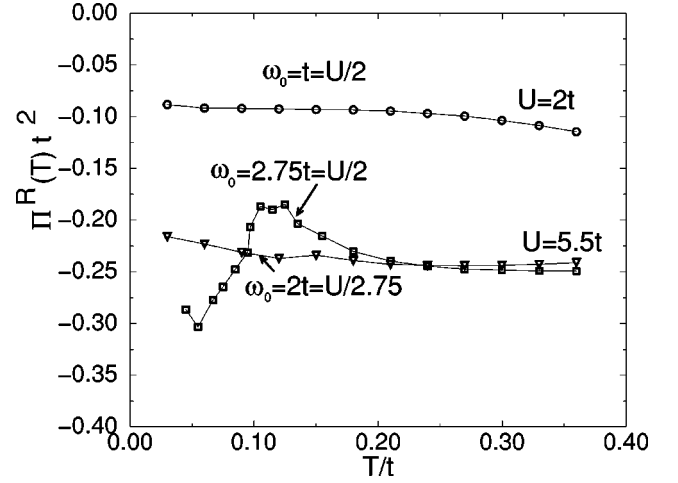


FIG. 2. Temperature dependence of the real part of the polarization for different frequencies and correlation strengths. Due to their coupling to electrons, the phonons undergo a frequency shift that is proportional to this polarization. Significant temperature dependence occurs when two conditions are simultaneously satisfied: (i) ω_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.

lifetime. This shift can be obtained from the poles of Eq. (3), which we denote by $\tilde{\omega}_{\mathbf{q}} = \omega_{\mathbf{q}} + i\Gamma_{\mathbf{q}}$. For weak electron-phonon coupling, the frequency shift is

$$\frac{\Delta \omega}{\omega_0} \equiv \frac{\omega_{\mathbf{q}} - \omega_0}{\omega_0} = \frac{g^2}{4} \Pi^R(\mathbf{q}, \omega_0), \quad (5)$$

where $\Pi^R(\mathbf{q}, \omega_0)$ denotes the real part of the polarization. The phonon damping is proportional to the imaginary part of the polarization. Figure 2 shows the temperature dependence of the real part of the polarization, $\Pi^R(\mathbf{q}=0, \omega_0)$, for different bare phonon frequencies, ω_0 .

Our DMFT calculations show that for frequencies close to $U/2$ and sufficiently strong interactions, the phonon frequency can have a nonmonotonic temperature dependence near the coherence temperature, T^* . From Fig. 2, we find that $T^* \approx 0.1t \sim 100$ K for $t \sim 0.1$ eV. However, this behavior 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 κ -(BEDT-TTF)₂X.⁶ Lin *et al.*⁷ have measured an anomalous softening below about 100 K of the Raman frequency shifts in the phonons, $\nu_9 = 505 \text{ cm}^{-1}$ and $\nu_{60}(B_{3g}) = 890 \text{ cm}^{-1}$ for κ -(BEDT-TTF)₂ Cu(SCN)₂ (see Fig. 5 in Ref. 7). The higher-frequency mode, $\nu_3 = 1478 \text{ cm}^{-1}$, also exhibits a strong (but monotonic) temperature dependence. Table I gives values of 0.3–1% for the magnitude of the total temperature dependence between about 10 and 300 K. Other phonons do not exhibit such a strong temperature dependence.¹⁴ Figure 2 and Eq. (5) imply that for a coupling $g \sim t$ the temperature dependence can be as large as 5% for $\omega_0 = U/2$ and of the order of 1% for larger or smaller frequencies. The values of g deduced below (see also Table I)

TABLE I. Parameters for three molecular phonons in κ -(BEDT-TTF)₂Cu(SCN)₂. The experimental values are taken from Ref. 22. The difference between the infrared frequency, ω_{IR} , and the Raman frequency, ω_R , and Eq. (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.¹⁹ $\Delta\omega_R(T)$ is the observed magnitude of the temperature dependence of the Raman-active mode between about 10 and 300 K. $\Delta\omega_{\text{SC}}$ is an estimate of the increase of the phonon frequency on entering the superconducting phase, based on Eq. (7).

Mode	Observed frequency (cm ⁻¹)			e - p coupling, g (eV)			
	Infrared (ω_{IR})	Raman (ω_R)	$\frac{\omega_R - \omega_{\text{IR}}}{\omega_R}$ (%)	est.	QC	$\frac{\Delta\omega_R(T)}{\omega_R}$ (%)	$\frac{\Delta\omega_{\text{SC}}}{\omega_0}$ (%)
ν_3	1276	1478	14	0.14	0.14	0.3	0.13
ν_9	431	505	15	0.07	0.08	1	0.7
ν_{60}	881	890	1	0.02	?	0.3	0.02

are consistent with $g \sim t$ if $t \sim 0.1$ eV; this is also reasonable.⁶ However, if $g \sim t \sim \omega_0$ this raises questions about vertex corrections to Eq. (4) and the contribution of electron-phonon coupling to the electronic self-energy. Yet the effects shown in Fig. 2 are at most a few percent and so we consider that effects that are higher order in g will be very small. In summary, our model can produce frequency shifts of the order of those observed (0.3–1 %) for reasonable parameter values. From the high-energy peak in the optical conductivity, it can be estimated^{4,5} that $U \sim 0.3$ eV = 2400 cm⁻¹. Hence, our model predicts the largest effects for phonons with frequencies of about 1200 cm⁻¹. However, the nonmonotonic temperature dependence is seen for a broader range of phonon frequencies than our model would predict.

We find even stronger effects for low-frequency phonons. In Fig. 3, the real part of the phonon self-energy¹⁵ is plotted for $\mathbf{q}=0$ 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.^{8,9}

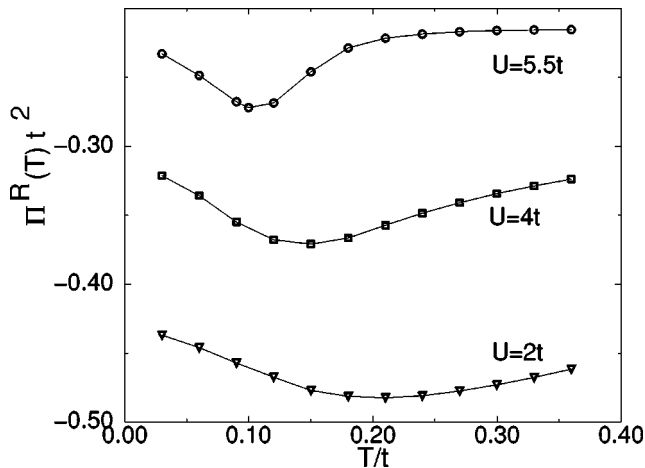


FIG. 3. Temperature dependence of the real part of the polarization for $\omega_0=0.05t$ and different values of U/t . A dip appears at the coherence temperature, T^* , and it becomes more sharply defined as the electron-electron interactions increase. The position of the dip shifts towards lower temperatures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

The velocity of ultrasonic waves that are propagating perpendicular to the layers was found to have a nonmonotonic 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 percent around 40 K. This softening becomes larger as the pressure is decreased and is about three times larger for κ -(BEDT-TTF)₂Cu[N(CN)₂]Br than κ -(BEDT-TTF)₂Cu(SCN)₂. Decreasing the pressure or changing the anion from Cu(SCN)₂ to 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_e increases and the metal-insulator transition is approached.²⁻⁴ 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. 8). However, caution is in order because further experiments¹⁶ find that the softening only occurs for waves propagating parallel to the layers when their polarization 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 κ -(BEDT-TTF)₂X is particularly amenable to studying 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 antisymmetric combination on the dimer. By parity conservation, the antisymmetric modes are infrared active and the symmetric modes are Raman active. If there is a Holstein model coupling for a single molecule, the Hamiltonian for a dimer is¹⁷

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

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 appear in Eq. (1).⁴ The bonding and antibonding orbitals associated with the dimer

are separated by $2t_0$, even in the presence of a Hubbard term. The Hamiltonian can be rewritten as

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

where $a_\pm = 1/\sqrt{2}(a_1 \pm a_2)$ 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 Eq. (1). It is the fluctuations in this term that produce the temperature dependence shown in Figs. 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 ω_0 . A second-order perturbative calculation¹⁷ predicts that for $\omega_0 \ll t_0$, the infrared frequency ω_{IR} will be smaller than the Raman frequency ($\omega_R = \omega_0$),

$$\frac{\omega_{\text{IR}} - \omega_R}{\omega_R} = -\frac{g^2}{2\omega_0 t_0}. \quad (6)$$

Table I lists the details of the measured frequency shifts for three different modes for κ -(BEDT-TTF)₂Cu(SCN)₂. For $t_0 = 0.3$ eV (Ref. 18), these values are used together with Eq. (6) to evaluate the electron-phonon coupling g . The values obtained are in reasonable agreement with those found in a modified neglect of differential overlap (MNDO) frozen phonon quantum chemistry calculation¹⁹ on a single BEDT-TTF molecule.

Zeyher and Zwicky²⁰ considered the frequency shift of phonons when they enter the superconducting phase. Within the framework of BCS theory, phonons with frequency ω_0 much smaller than the Fermi energy and much larger than the superconducting gap Δ will harden by an amount

$$\frac{\omega_s - \omega_R}{\omega_0} = \frac{8g^2 N(0)}{\omega_0} \left(\frac{\Delta}{\omega_0} \right)^2 \ln \left(\frac{\omega_0}{\Delta} \right), \quad (7)$$

where $N(0)$ is the density of states per spin at the Fermi energy. There should be no shift in the frequency of the infrared-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 I. Eldridge *et al.*¹⁴ found that in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, the $\nu_{60}(B_{3g})$ mode at 890 cm^{-1} hardened by about 0.2% on entering the superconducting phase. A shift in this mode was not detected in κ -(BEDT-TTF)₂Cu(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 Eq. (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 acoustic phonons the softening will scale like $(\omega_0/\Delta)^2$ 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 bandwidth 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 that is much less than the bandwidth.

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