Temperature-dependent hybridization gaps: A cause of phonon anomalies in f electron systems?

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Abstract. There is evidence that a number of heavy-fermion/mixed-valent materials show strongly renormalized hybridization gaps either at the Fermi-energy or close to the Fermi-energy. In the former case, a heavy-fermion semiconducting state ensues and in the later case, the system remains metallic at low temperatures. Due to the temperature-dependence of the electronic correlations, the magnitudes of the hybridization gaps decrease with increasing temperatures. The existence of a temperature-dependent low-energy electronic energy scale opens up the possibility that the Born-Oppenheimer approximation may fail and that there may be a resonant coupling between the phonons and the electronic excitations. It is argued that such a mechanism may be the cause of the anomalous phonon mode observed in α-uranium at high temperatures.

1. Introduction
The low temperature state of heavy fermion semiconductors or Kondo insulators are commonly described by a hybridization gap model in which the hybridization gap is strongly reduced due to the presence of strong electronic correlations[1]. Archetypes of this class of materials are given by Ce₃Bi₄Pt₃[2], SmB₆[3] and YbB₁₂[4]. The gap has been observed in Ce₃Bi₄Pt₃ by inelastic neutron scattering experiments[5, 6], optical conductivity[7, 8] and photoemission measurements[9, 10]. Substitutional doping rapidly closes the gap[11, 12] which illustrates that the gap has a coherent character as is expected for a hybridization gap[13]. Furthermore, measurements of the gap in Ce₃Bi₄Pt₃ show that it is strongly temperature dependent[14] which is in agreement with the theory. In these semiconducting materials, the gap opens up at the Fermi-energy. Low-lying hybridization gaps or pseudogaps have been observed in materials which are always metallic such as YbFe₄Sb₁₂[15], CeRu₄Sb₁₂[15] and UPd₄Al₃[16]. The existence of either pseudo-gaps or gaps in the electronic spectrum with magnitudes in the range 12 to 50 meV raises the possibility of the existence of excitations which through resonant interactions have mixed electronic and phonon character. In particular, this mixing could result in the softening of the optic phonon spectrum and the formation of more than three modes for each lattice degree of freedom[17, 18].

The phonon spectrum of α-uranium shows a marked harmonic softening at high temperatures[19, 20] and also shows the formation of a new mode[21, 22] at temperatures around 450 K. However, those authors argue that the anomalies are due to the formation of intrinsically localized modes. Intrinsically Localized Modes (ILMs) are persistent oscillatory and spatially localized excitations of homogeneous lattices that are stabilized by strong anharmonicity[23].

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Such modes have been extensively studied in classical one-dimensional lattices via numerical simulations[24, 25]. In the classical limit, these excitations should give rise to a broad continuous spectral density which is in direct contrast to the discrete nature of the observed spectrum[21]. This discrepancy can be resolved by quantizing the internal degree of freedom of the ILM, in which case, the observed excitation could correspond to the lowest non-trivial ILM that has the quantum number \( n = 2 \). However, an investigation of quantized ILMs[26] shows that the ILM should exist for all momentum transfers, and is not restricted to a small range of momentum transfers as found in the experiments[21, 22]. Therefore, due to the harmonic nature of the lattice[20] and due to the localized nature of the excitation in momentum space, the experimental measurements are not fully in accord with the interpretation in terms of ILMs. Hence, in this manuscript, we shall indicate how the existence of a small temperature-dependent hybridization gap can result in the softening of the phonon modes and how it may lead to the formation of a new breathing mode.

2. Calculation and Results
The system is described by the Anderson Lattice Hamiltonian which includes an \( f \)-electron phonon interaction. The on-site Coulomb interaction is treated within the mean-field slave boson approximation[6], which at low temperatures produces a coherent renormalized band. The coherent quasiparticle band is characterized by a renormalized temperature-dependent hybridization matrix element \( V(T) \) and an \( f \)-level energy \( E_f(T) \) which is shifted close to the Fermi-energy. The resulting system of renormalized quasiparticles and phonons is described by

\[
\hat{H} = \sum_{i,\sigma} E_f(T) f_{i\sigma}^\dagger f_{i\sigma} + \sum_{k,\sigma} \epsilon_k d_{k\sigma}^\dagger d_{k\sigma} + \sum_{k,\sigma} \left( V(T) f_{k\sigma}^\dagger d_{k\sigma} + V(T)^* d_{k\sigma}^\dagger f_{k\sigma} \right) \\
+ \sum_{q,\gamma} \hbar \omega_{q\gamma} a_{q\gamma}^\dagger a_{q\gamma} + \sum_{k,\gamma} \lambda_{q\gamma} \left( a_{q\gamma}^\dagger + a_{-q\gamma} \right) f_{k+q\sigma}^\dagger f_{k\sigma} 
\]

Figure 1. The real (blue line) and the imaginary parts (red line) of the polarization part \( 2\omega_q \Pi_q(\omega) \) in units of (eV)\(^2\) versus frequency (in units of eV), for \( q = (\pi, \pi, \pi) \). The renormalized phonon frequency is given by the intersection of the line \( 2\omega_q \Pi_q(\omega) \) with the parabola \( \omega^2 - \omega_q^2 \) (dashed line). The plot shows that the renormalized phonon frequency exhibits a significant softening when the bare frequency \( \omega_q \) is comparable to the indirect gap.
phonon with wave vector $q$ and polarization $\gamma$. The phonon propagator is calculated from the Dyson equation

$$D_q(\omega) = D^0_q(\omega) + D^0_q(\omega) \Pi_q(\omega) D_q(\omega)$$ (2)

where the unperturbed phonon propagator is given by

$$D^0_{\gamma\gamma}(\omega) = \frac{2 \hbar \omega_{\gamma\gamma}}{\hbar^2 \omega^2 - \hbar^2 \omega_{\gamma\gamma}^2}$$ (3)

and the polarization part $\Pi_q(\omega)$ is calculated to order $\lambda^2 q^2$. The polarization part shows a dramatic low frequency variation for wave vectors $q$ near the boundary of the Brillouin zone. The frequency dependence of the real and the imaginary parts of the polarization part are shown in fig.(1). The characteristic energy scale of the peaks in the real part and the threshold of the imaginary part is given by the indirect hybridization gap[6]. The renormalized phonon frequencies are given by the intersection of the curve $2\hbar \omega_{\gamma\gamma} \Re \Pi_q(\omega)$ with the parabola $\hbar^2 (\omega^2 - \omega_{\gamma\gamma}^2)$. The lifetime of the excitation is governed by $2\hbar \omega_{\gamma\gamma} \Im \Pi_q(\omega)$. It is seen that as the temperature is increased and the hybridization gap decreases towards the optic phonon frequency, the electron-phonon coupling can result in a softening of the phonon spectrum. For phonon frequencies smaller than the indirect gap, the curves may have more than one intersection. In this case, resonant mixing occurs between the electronic excitations and the optic phonon modes which leads to the formation of a new broad mode at high energies.

In summary we have argued that, in an f-electron system with a sufficiently small hybridization gap or pseudo-gap, the electron-phonon interactions may couple the electronic excitations with the phonon modes. If, as the temperature is decreased, the hybridization gap is lowered towards the optic phonon frequency, then the optic modes are expected to soften with increasing temperature. As the hybridization gap is further reduced below the optic phonon frequency, one expects that the electronic excitations will resonantly mix with the phonons resulting in a splitting of the optic modes into two branches. The predictions of this mechanism are consistent with experimental results on $\alpha$-uranium[19, 21], even though at the present time there is no direct experimental evidence for the existence of a hybridization pseudo-gap. The proposed mechanism could be active in the large class of materials which are known to exhibit small hybridization gaps.

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3. References

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