RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Pseudoexcitons in mixed-valence metals

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(Received 25 July 1988)

Recent neutron scattering studies of the phonon dispersion relations of α-Ce and $CePd_3$ have revealed a mode splitting in the (100) LA branch around the spin-fluctuation temperature. It is shown that this behavior could be caused by the mixing of LA phonons with excitonlike entities formed by localized f holes and broad-band electrons.

Since hydrostatic pressure induces drastic changes in the properties of Ce and some intermetallic compounds of Ce, Sm, and Yb, it is expected that acoustic phonons should interact strongly with the f-shell electrons on the rare-earth ions. A considerable amount of experimental and theoretical effort has been spent to elucidate this interaction in the past decade.[1-13] It has been found that acoustic phonons in these so-called mixed-valence materials are softened and their linewidths are broadened, due to charge fluctuations in a narrow band of hybridized f and conduction electrons. Recently, a new and puzzling phenomenon has been observed independently by two groups. In a preliminary study of α-Ce Stassis and coworkers have found that the acoustic-phonon mode in the (100) direction splits in the middle of the Brillouin zone as if it were mixed with an invisible mode at a frequency of 2 THz or an energy of 8.3 meV.[12] The experiment was done at 90 K, and the result has not been published pending further measurements over a range of temperature. In the meantime, Severing *et al.* have reported a similar finding in $CePd_3$.[13] At temperatures below the spin-fluctuation temperature ($\sim$140 K) of this material, the LA phonons are softened, as was seen in SmS systems.[1-4] At 200–300 K the (100) mode splits near the zone boundary in the same manner as seen in α-Ce, and the invisible mode has an energy around 10 meV. We suggest that the mode splitting signals new physics not contained in the previous theoretical treatments, and we offer an explanation in this paper.

Generally speaking the physical properties of mixed-valence and heavy-electron systems differ significantly depending on whether the temperature is above or below a characteristic temperature, commonly called spin-fluctuation temperature T_f.[14] Below T_f the f electrons, about one per rare-earth site in Ce systems, are in bandlike states and behave like a Fermi liquid with high effective mass. Above T_f the f electrons are localized and provide rapidly fluctuating local moments. The transition may be continuous, as in $CePd_3$, or may be accompanied by an abrupt volume change, as in Ce. The physics of the transition is not entirely clear, but it is generally agreed that T_f measures the effective position of the f level from the Fermi energy.[14(b)] This amount of basic information is sufficient for the discussion of LA phonon anomaly.

As in previous theoretical works we use the same Hamiltonian for the interaction between the electron systems and LA phonons, i.e., that the phonons promote electrons from the f shell to the d band and vice versa. The interaction Hamiltonian is written as[5]

$$H_{e\text{-ph}}=\frac{1}{\sqrt{N}}\sum_i\sum_{\mathbf{k},\mathbf{q}}M(\mathbf{q})[f_i^\dagger d_{\mathbf{k}-\mathbf{q}}e^{-i\mathbf{k}\cdot\mathbf{R}_i}+d_{\mathbf{k}+\mathbf{q}}^\dagger f_i e^{i\mathbf{k}\cdot\mathbf{R}_i}](a_{\mathbf{q}}+a_{-\mathbf{q}}^\dagger), \quad (1)$$

where f_i is the annihilation operator of an f electron on site $\mathbf{R}_i$ and $d_{\mathbf{k}}$ is that for a band electron in momentum state $\mathbf{k}$, $a_{\mathbf{q}}$, and $a_{\mathbf{q}}^\dagger$ are the LA phonon operators in momentum state $\mathbf{q}$, and N is the number of Ce sites in the lattice. The form of the matrix element $M(\mathbf{q})$ has been calculated in detail in Refs. 5–9. The propagator $D(\mathbf{q},\omega)$ for the LA phonon of momentum $\mathbf{q}$ satisfies the Dyson equation

$$D^{-1}(\mathbf{q},\omega)=(\omega^2-\omega_{\mathbf{q}}^2)/2\omega_{\mathbf{q}}-\Pi(\mathbf{q},\omega), \quad (2)$$

where $\omega_{\mathbf{q}}$ is the phonon frequency in absence of the d-f charge-fluctuation interaction in Eq. (1), and $\Pi(\mathbf{q},\omega)$ is the phonon self-energy due to this interaction:

$$\Pi(\mathbf{q},\omega)=N^{-1}\sum_{i,j}|M(\mathbf{q})|^2\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\int_0^\infty e^{i\omega t}\langle Tf_i^\dagger(t)d_{\mathbf{k}}(t)d_{\mathbf{k}'}^\dagger(0)f_j(0)\rangle dt e^{i(\mathbf{k}\cdot\mathbf{R}_i-\mathbf{k}'\cdot\mathbf{R}_j)}, \quad (3)$$

where T is the time ordering operator. In the Fermi-liquid phase the quasiparticles are mixed d and f states in a narrow, partially filled band. In previous theoretical works the phonon self-energy is calculated in the band representation, with the result that the real part of $\Pi(\mathbf{q},\omega)$ gives a softening of the phonon energy and the imaginary part gives a line broadening. There is good agreement between theory and experiment in many systems, such as SmS and $CePd_3$ at low temperatures. In both cases the electron-phonon interaction is the strongest for LA phonons in the (100) direction.[5-8,13]

We now consider what happens above T_f when the f electrons are localized. The promotion of an f electron into the d band leaves behind a localized attractive Coulomb potential to the band electrons. The latter responds by forming a screening cloud around the f hole,

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and the dynamics of the screening process has been thoroughly studied nearly two decades ago as the edge singularity problem in the optical absorption of deep core electrons.[15-17] In the present situation the LA phonon plays the role of the photon and the f electron, which is more tightly bound than d electrons, plays the role of the core electron. The importance of d-f Coulomb correlation in mixed-valence and heavy-electron materials has been emphasized by the present author.[18-21]

It has been shown in Refs. 15–17 that the phonon self-energy $\Pi(\mathbf{q},\omega)$ at zero temperature is

$$\Pi(\mathbf{q},\omega)=A(\mathbf{q})(\omega-\omega_0)^{-\alpha'}, \tag{4}$$

where $\omega_0=\mu-\varepsilon_f$ is the energy of the f level measured from the Fermi level. The quantity ε_f contains all appropriate renormalizations and is very close to the Fermi energy.[14(b)] The spectrum has a power-law singularity which arises from the sharp change of electron population at the Fermi level, and the exponent $\alpha'=2\delta/\pi-(\delta/\pi)^2$ where δ is the d-electron phase shift at the Fermi level when scattered by the f-hole potential. We do not know the precise value of α' except that it is bounded by 0 and $\frac{3}{4}$. The factor $A(\mathbf{q})$ contains the matrix-element square and other d-band parameters. We call the entity formed by the f hole and its screening cloud a pseudoexciton to distinguish it from real excitons in semiconductors. It is not a bound state, but it has the appearance of a mode with energy ω_0 because of the edge singularity. It leads only a transient existence and evolves into a static screening cloud in the long-time limit.

Since we are interested in the phonon renormalization at temperatures of the order of ω_0, we need to work out the self-energy $\Pi(\mathbf{q},\omega)$ at finite temperatures by extending a calculation of the photoemission spectrum in Ref. 19. The result is

$$\Pi(q,\omega)=\frac{A(\mathbf{q})}{2\Gamma(\alpha')}(\beta/\pi)^{\alpha'-1}\frac{e^{\beta x}+e^{-i\pi\alpha'}}{\cosh(\beta x)+\cos(\pi\alpha')}\times\int_0^\beta e^{-x\tau}[\sin(\pi\tau/\beta)]^{\alpha'-1}d\tau, \tag{5}$$

where β is the inverse temperature and $x=\omega-\omega_0$. The power-law singularity is broadened by excitations near the Fermi level into a round peak whose width is measured by the temperature. This result is put into Eq. (2) to calculate the phonon line shape, which is the imaginary part of $D(\mathbf{q},\omega)$.

In Fig. 1 we show the evolution of the line shape over a range of phonon energies around ω_0 and at three temperatures. All energies as well as temperature are measured in units of ω_0, which is taken as the definition of T_f for our purpose. No attempt is made to fit the phonon dispersion curve or line shape of any material. Instead, we choose to present the physics in its rudimentary form with a minimum number of parameters. We give the phonon an intrinsic linewidth $\Gamma=0.1\omega_0$ to simulate experimental resolution and other scattering effects. A constant electron-phonon matrix element is chosen to give a mode splitting of $0.1\omega_0$ at temperature equal to T_f and $\omega_q=\omega_0$. The exponent α' is taken as 0.7, and the results are not very sensitive to α'. In cases where the mode is split, the peak with lower energy is noticeably narrower. This behavior is intrinsic because a larger Γ would broaden both peaks by the same amount. At higher temperatures the mode split-

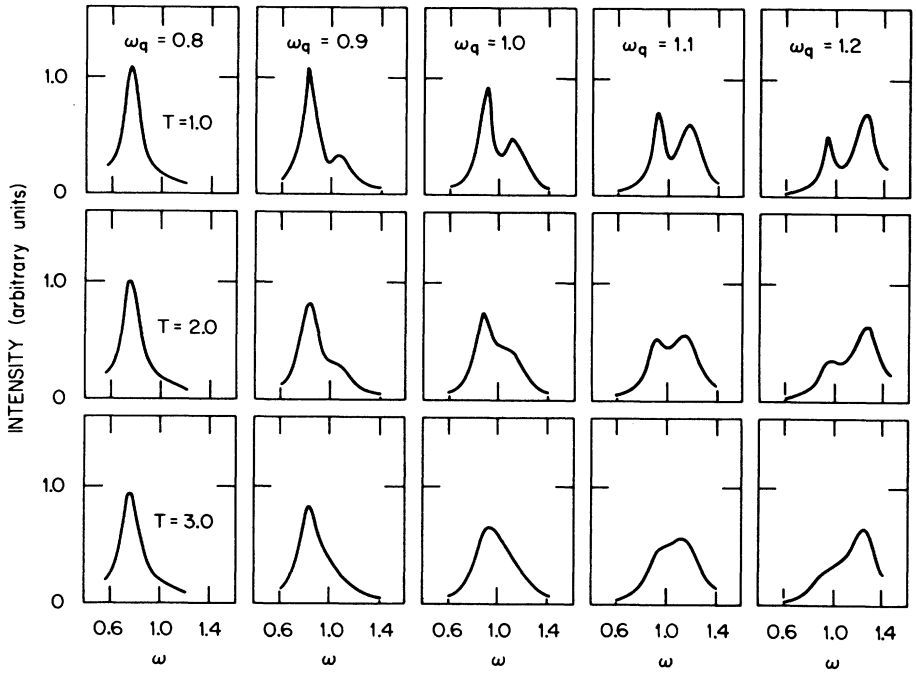

FIG. 1. Line shapes of LA phonons in the energy and temperature range where mode splitting occurs. All energies as well as temperatures are in units of ω_0, which is a measure of the spin-fluctuation temperature.

ting becomes less discernable and eventually disappears when the combined width of the phonon and the pseudoexciton far exceeds the size of the matrix element. Only the asymmetry in line shape hints at the presence of some unusual effect.

In Fig. 2 we show the evolution of the peak position as phonon energy and temperature vary. This is not a dispersion curve of the mixed mode because the horizonal axis is the unnormalized phonon energy and not the momentum. Nevertheless, it does not show qualitatively the shape of the LA phonon disperison curve near the mode crossing point. For temperatures between T_f and $2T_f$ the peak position is insensitive to temperature, but at higher temperatures when the splitting disappears, the peak position follows an S-shaped curve very similar to the results of existing theories. Thus, unless one studies the right material in the right temperature range with sufficiently high resolution, the mode splitting can be easily missed and one would be led to conclude that existing theories are adequate to explain the data.

The above theoretical predictions seem to be consistent with experimental findings. Because the experiments were not designed for the purpose of determining the phonon line shape, it seems premature to attempt quantitative comparison between theory and experiment. Careful measurements in the interesting energy and temperature range will be very helpful. Notice that our definition of the spin fluctuation temperature puts $T_f = 96$ K for α-Ce and 120 K for $CePd_3$. For the latter material our value for T_f is very close to the temperature of maximum resistivity $T_{max} = 140$ K.

One important ingredient is still missing in Eq. (5). This concerns the f-level broadening, which is a necessary consequence of the transition from band to local f states.[20,21] One must fold this level width into Eq. (5) before comparing theoretical with experimental linewidths and line shapes. Since the level width is temperature dependent, the predicted behavior shown in the figures is only valid qualitatively.

The basic physical picture presented here, that mixed-valence materials have an f level at approximately T_f below the Fermi level, has been called to question lately.[14] It has been shown by Bickers and co-workers[22,23] that the physical properties of Ce impurities can be explained as manifestations of a spin-fluctuation resonance state, which is a localized state above but very close to the Fermi level. This model is the modern version of the Kondo anomaly, and the extension of this theory to a lattice of f sites may explain the anomalous properties of mixed-valence and heavy-electron materials.[24] Our theory of phonon anomaly is not sensitive to the detail of the physical picture, because putting an electron in an empty local state also creates a local screening cloud with the same dynamical properties. Like the band picture, the spin-fluctuation resonance level has been shown to broaden with increasing temperature.[22] At the present state of theoretical development it does not seem possible to distinguish between the two models by studying the phonon anomaly.

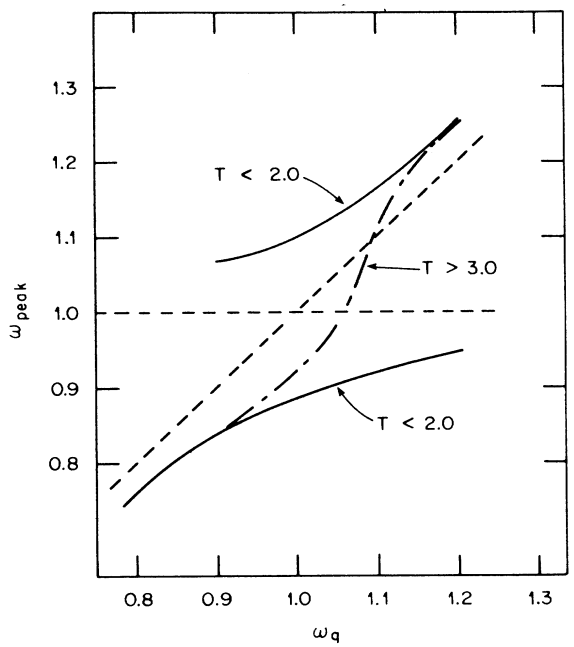

FIG. 2. The evolution of peak position as a function of unnormalized phonon energy and temperature. It gives qualitatively the shape of the LA phonon dispersion curve near where mode splitting occurs. All frequencies in units of ω_0.

Unlike real excitons, it is difficult to observe pseudoexcitons by infrared absorption because the signal can be easily obscured by the large Drude background.[25,26] This leaves the longitudinal acoustic phonon as the only effective tool to probe its properties. Other possible manifestations of pseudoexciton effects remain to be investigated.

The author would like to thank C. Stassis for suggesting the investigation. Helpful discussions with H. A. Mook are gratefully acknowledged. The research is sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-85OR21400 with Martin Marietta Energy Systems, Inc.

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