Anomalies caused in phonon spectra by charge density fluctuations

M. I. Katsnel'son and A. V. Trefilov
Institute of Metal Physics, Academy of Sciences of the USSR, Sverdlovsk; I. V. Kurchatov Institute of Atomic Energy, Moscow

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Charge density fluctuations cause anomalies in the phonon spectra and lattice properties of systems which have narrow peaks in the state density near the Fermi level (in particular, compounds with the A15 structure and heavy-fermion systems). These anomalies should intensify anharmonic effects. An experimental study of these features might explain the nature of the peaks in the state density in heavy-fermion systems.

Compounds having very narrow peaks in the electron state density, $N(E)$, near the Fermi level E_F have recently become the subject of active research. These compounds include, in particular, high-temperature superconductors with the A15 structure[1,2] and heavy-fermion systems.[3,4] Many of the physical properties of these systems exhibit an unusual behavior. There are anomalously large electron components of the heat capacity C and the paramagnetic susceptibility χ, and there are substantial deviations from a monotonic temperature dependence of C, χ, the thermal expansion, the resistance, etc. Various mechanisms have been considered in an effort to explain these anomalies. For the A15 compounds, the possibilities considered have been structural features in their one-electron spectra due to the lattice symmetry,[5] a polaron effect,[6] and a strong electron-phonon interaction. In the case of heavy-fermion systems, there has been a study of a "Kondo lattice" model (Ref. 3, for example). When there are narrow peaks in $N(E)$ near E_F, the electron and lattice properties of the metal acquire anomalous components from fluctuations of the charge density, e.g., a strong frequency dispersion of the dielectric constant.[8] This effect is extremely widespread, and it should apparently be seen (along with the mechanisms listed above) in all systems with narrow peaks in $N(E)$ near E_F, although it will vary in prominence. We wish to emphasize that the nonmonotonic temperature dependence of χ, C/T (with a maximum[4]), and the elastic moduli (with a minimum; see, for example, the data[3] on $CeSn_3$) can be attributed to anomalous contributions from charge density fluctuations.[8] In the present letter we show that the electron-phonon interaction with charge density fluctuations leads to a significant intensification of the anomalies in the phonon spectra and the lattice properties.

A distinctive feature of high-temperature superconductors with the A15 structure and of heavy-fermion systems is the existence of peaks in $N(E)$ for which Δ (the distance to E_F) and the width Γ are comparable to typical phonon frequencies. A question that arises in this situation is whether the adiabatic approximation is applicable. The "dangerous" contribution to the phonon eigenenergy part $\Sigma_{ph}(\mathbf{q}\omega)$ (which determines the frequency shift and the attenuation of the phonons) is $-\lambda^2\Pi(\mathbf{q}\omega)$,

where $\Pi(\mathbf{q}\omega)$ is the contribution of transitions from the narrow peak in $N(E)$ to E_F to the electron polarization operator. In the random-phase approximation this contribution is[9]

$$\Pi(\mathbf{q}\omega) \approx B(\mathbf{q}) \ln(E_F^2/\Delta^2 - \omega^2 - i0),$$
$$B(\mathbf{q}) = \sum_{\mu} |\langle \nu | \exp i\mathbf{q}\mathbf{r} | \mu \rangle|^2 \delta(\epsilon_\mu - E_F), \tag{1}$$

where $|\nu\rangle$ are the electron states which form the peak of width $\Gamma \ll \Delta$, and λ is the constant of the electron-phonon interaction, which corresponds to the emission (absorption) of a phonon accompanied by a simultaneous transition of an electron from the peak to E_F ($\nu \rightleftarrows \mu$). As was shown in Ref. 10, this electron-phonon interaction is the most important interaction in the related situation of an intermediate valence.

Although (1) cannot be analyzed in the adiabatic approximation[11] [$\Pi(\mathbf{q}\omega) \to \Pi(\mathbf{q}0)$], this entire contribution is small in comparison with the total value $\Sigma_{\text{ph}}(\mathbf{q}0)$, because the wave functions $|\nu\rangle$ and $|\mu\rangle$ overlap only slightly; i.e., in the case under consideration, the adiabatic approximation will be valid not because the ordinary adiabatic parameter[11] is small but because this overlap is small. By virtue of (1), the contribution of the dangerous transitions to $\hat{\Sigma}_{\text{ph}}$ leads to a softening of the phonon spectrum: $\delta\omega \sim \ln\Delta$. Since $\Pi(\mathbf{q}\omega) \sim \mathbf{q}^2$ in the limit $\mathbf{q} \to 0$, there is no corresponding contribution to the elastic moduli B_{ik}. In the acoustic region ($\omega \sim q$), the softening of the phonon spectra due to the charge density of fluctuations, $\delta\omega \sim \ln\Delta$, is therefore due to an exchange-correlation contribution,[8] which becomes less singular ($\delta\omega \sim \Delta\ln\Delta$; Ref. 8) at larger values of q, but a contribution $\delta\omega \sim \ln\Delta$, discussed above, simultaneously arises. As a result, "breaks" should be observed in the phonon spectra at small values of q to the extent to which the effects discussed above are important, while at values of q on the order of the reciprocal lattice vector we should see dips. This behavior of the phonon spectra is characteristic of A15 systems.[12] We wish to emphasize that even sharper anomalies should be observed in the Grüneisen parameters $\tilde{\gamma}_{\mathbf{q}} = -[(d\ln\omega_{\mathbf{q}})/(d\ln V)] \sim \Delta^{-1}$ (V is the volume).

In the limit $\omega \to \Delta \gg \Gamma$, the problem of determining the singular contribution to $\Pi(\mathbf{q}\omega)$ is formally equivalent to the problem of an "edge singularity" in x-ray spectra, where higher orders of a perturbation theory in the electron-electron interaction must be taken into account.[9] According to Ref. 9, we then replace (1) by

$$\Pi(\mathbf{q}\omega) = \sum_l A_l(\mathbf{q}) \frac{1}{\alpha_l} \left[\left(\frac{E_F}{\Delta - \omega} \right)^{\alpha_l} + \left(\frac{E_F}{\Delta + \omega} \right)^{\alpha_l} - 2 \right],$$
$$\alpha_l = \frac{2}{\pi} \delta_l - 2 \sum_{l=0}^{\infty} (2l+1) \left(\frac{\delta_l}{\pi} \right)^2 \tag{2}$$

Here δ_l is the phase shift in the scattering by the hole potential formed as an electron goes from a peak in $N(E)$ to the Fermi level, and the coefficients $A_l(q)$ are associated with the screening effect of the electrons on E_F with an orbital angular momentum l. In the d- of f-resonance model, in which only scattering with a single value $l = 2$ or 3 is

taken into account, we find from the Friedel sum rule $(2/\pi)\Sigma_l(2l+1)\delta_l = 1$ that we have $\alpha = [2(2l+1)]^{-1}$, i.e., that α is greater than 0 but small. In the case of strong s scattering (a small ion radius), α can be much larger: $\alpha \approx 1/2$. The contribution of (2) to the phonon attenuation γ_q is determined by the quantity

$$\mathrm{Im}\,\Pi(\mathbf{q}\omega_{\mathbf{q}}) \sim |\omega_{\mathbf{q}} - \Delta|^{-\alpha}\theta(\omega_{\mathbf{q}} - \Delta). \tag{3}$$

It follows from (2) and (3) that at $\alpha > 0$ the attenuation $\gamma_{\mathbf{q}}$ and also the phonon state density $g(\omega)$ increase as $\omega \to \Delta$. There is a singular contribution to $g(\omega) \sim |\omega - \Delta|^{-\alpha}$, as $\omega \to \Delta$. We believe that an experimental study of the phonon attenuation would be of particular interest for heavy-fermion systems, since it might tell us whether the peak in $N(E)$ persists up to high temperatures or whether it is a low-temperature peak, as would follow from the suggestion that it is of a purely Kondo nature.[3] It is clear from this analysis that the conclusion that there is strong attenuation at $\omega > \Delta$, $\omega \to \Delta$ applies not only to phonons but also to other excitations in the corresponding frequency interval, including, for example, local excitations associated with a splitting of the f level in a crystal field. We note in this connection that it has been established experimentally that local excitations in $CeAl_3$ (a heavy-fermion system) are strongly attenuated at temperatures up to room temperature, in contrast with the situation in $PrAl_3$ and $NdAl_3$ (Ref. 13). This circumstance might be explained on the basis of (3), under the assumption that one of the sublevels of the f level in $CeAl_3$ is near E_F, so that the energy of the local excitation is equal to Δ (the distance from the other sublevel to E_F). This assumption seems logical for heavy-fermion systems.

Incorporating the electron-phonon interaction and the charge density fluctuations leads to a contribution to the Ω potential:

$$\delta\Omega = -\frac{1}{2}\lambda^2 T \sum_{\mathbf{q}\,\omega} \Pi(\mathbf{q}, i\omega)\frac{\omega_{\mathbf{q}}^2}{\omega_{\mathbf{q}}^2 + \omega^2},\quad \omega = 2\pi nT,\ n = 0, \pm 1. \tag{4}$$

Using (1), we then find

$$\delta\Omega = -\frac{1}{2}\lambda^2 \Sigma_{\mathbf{q}} B(\mathbf{q})\omega_{\mathbf{q}}^2\left(\frac{1}{2\omega_{\mathbf{q}}}\coth\frac{\omega_{\mathbf{q}}}{2T}\ln\left|\frac{E_F^2}{\Delta^2 - \omega_{\mathbf{q}}^2}\right| + \int_{\Delta}^{\infty}\frac{dx}{\omega_{\mathbf{q}}^2 - x^2}\coth\frac{x}{2T}\right)$$

$$\approx \begin{cases} \dfrac{\lambda^2}{2}\Sigma_{\mathbf{q}} B(\mathbf{q})\omega_{\mathbf{q}}\ln(E_F/\Delta + \omega_{\mathbf{q}}), & T = 0 \\ -\lambda^2 T\Sigma_{\mathbf{q}} B(\mathbf{q})\ln(E_F/\Delta), & T \gg \Delta, \Theta_D \end{cases} \tag{5}$$

where Θ_D is the Debye temperature. It follows from (5) that anharmonic effects, including an anharmonicity of the potential, are large at small values of Δ, since each additional variation $\delta\Omega$ with respect to displacements leads to an intensification of the singularity. The conclusion that there are strong anharmonic effects in compounds with the A15 structure was reached in Ref. 7 on the basis of other considerations. In

the present letter, in contrast with Ref. 7, we have not assumed that the electron-phonon interaction is very large.

As the temperature is raised, the peaks in $N(E)$ should broaden,[9] causing an increase in the effective values of Δ: $d\Delta/dT>0$. The softening of the phonon spectra should thus be intensified as the temperature is lowered; i.e., there should be an "intergrowth" of the peaks in $g(\omega)$ at $\omega\sim\Delta$ [at high values of T, these features will probably be blurred by the broadening of the peaks in $N(E)$]. Interestingly, the anharmonic contribution to the lattice heat capacity is negative (if $|(d\ln\Delta)/(d\ln T)|\lesssim 1$), according to (5), in agreement with experimental data on A15 compounds.[14]

A calculation of the mean square displacement $\langle x^2(T)\rangle$, which can be carried out by analogy with the calculation of $\delta\Omega$, leads to the result

$$\delta\langle x^2(T)\rangle \approx \begin{cases} \dfrac{\lambda^2}{2}\sum\limits_{\mathbf{q}}\dfrac{B(\mathbf{q})}{\omega_{\mathbf{q}}+\Delta}, & T=0 \\ 2\lambda^2 T\sum\limits_{\mathbf{q}}\dfrac{B(\mathbf{q})}{\omega_{\mathbf{q}}^2}\ln\left(\dfrac{E_F}{\Delta}\right), & T\gg\Delta,\Theta_D\,. \end{cases} \tag{6}$$

It follows from (6) that at $\Delta\ll E_F$ the average $\langle x^2\rangle$ is anomalously high; by virtue of the Lindemann criterion, this result should lead to a decrease in the melting point T_m. Such an effect might cause, for example, an admixture of impurities with narrow quasilocal levels near E_F of the matrix. There is the possibility that the results found regarding the increase in $\langle x^2\rangle$ and the intensification of anharmonic effects at small values of Δ (so that the anomalous contributions to $\langle x^4\rangle$ are far greater than those to $\langle x^2\rangle^2$) explain the very large displacements of the V atoms that are observed[15] in V_3Si. According to Ref. 15, this behavior would correspond, in terms of an interatomic potential, to a two-minimum potential.

It follows from this analysis that an experimental study of lattice properties [phonon attenuation, $g(\omega)$, the Debye-Waller factor, and T_m] of compounds with narrow peaks in $N(E)$ near E_F, in particular, heavy-fermion systems, would be of significant interest, especially upon variations in external parameters that would change Δ (the pressure, a uniaxial deformation, or an impurity concentration).

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