PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 28, NUMBER 4 — 15 AUGUST 1983

Possibility of acoustic plasmons in mixed-valence metals and their interaction with phonons

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(Received 2 March 1983)

Mixed-valence metals are characterized by the presence of both the very heavy f and the light s-d electrons near the Fermi surface. These conditions are propitious for the existence of the plasmon branch with acoustic character. We derive the dispersion relation for such modes and consider their interaction with the phonons of the lattice. The longitudinal sound velocity is shown to be strongly reduced by the interaction, as is experimentally observed. We propose that ultrasonic experiments be used to directly observe the acoustic plasmons.

I. INTRODUCTION

The possibility of plasmon excitations which exhibit acoustic behavior at long wavelengths ($\omega \to 0$ as $k \to 0$) for metals in which two species of electrons, one of mass much heavier than the other, has been discussed by previous workers.[1] The lighter electrons screen the long-wavelength components of the Coulomb field due to the heavier electrons leading to acoustic dispersion of a mode in which the two species move in phase with each other (like the longitudinal-acoustic phonons of a metal), as well as the usual plasmon mode in which they move out of phase. Most of the treatments have been directed to the case of transition metals.[2–7] None of these excitations have been observed in transition metals, probably because the ratio of the d-electron to the s-electron masses is typically only 2—4, which makes such excitations very ill defined. This follows from the fact, which is easily shown, that the Landau damping rate of the acoustic plasmon mode is proportional, at long wavelengths, to $(v_h/v_l)^{1/2}$ of its energy, where v_l is the Fermi velocity of the light electrons and v_h is the Fermi velocity of the heavy electrons. This means that there would only be a broad shift in the dielectric response to lower frequencies due to the mutual screening of the two species.

We proposed earlier[8] that rare-earth and actinide mixed-valence metals are a good place to look for the acoustic plasmons. The phenomenology[8,9] of these materials is that they behave as two-component Fermi liquids—one of which, associated primarily with the f electrons, is 2 orders of magnitude heavier than the other, which is associated primarily with the s-d electrons.

All the treatments of acoustic plasmons in metals have treated the dielectric response for the electrons as diagonal and have neglected local-field corrections, even when including the effects of hybridization on the band structure.[5] Also coupling of these modes to the longitudinal-acoustic phonon modes has, in general, been neglected.

The primary new result discussed in this paper is a calculation of the coupling of the acoustic plasmon mode to phonons, which demonstrates how they both retain their acoustic character, as they must, from general translational invariance criteria. We point out here that there are really two translational invariance conditions if the latter is included, namely the overall translational invariance of the whole crystal (which leads to the acoustic sum rule), and the translational invariance of the f electrons relative to the lattice, when the conduction electrons are free to screen the resulting charge displacement. These two invariance conditions result in the appearance of two acoustic modes in the long-wavelength limit. We calculate the modification of the velocities and shift in the spectral weights due to this coupling. We think this is a worthwhile exercise since a good method to detect the new mode may be through ultrasonic experiments. We start, however, with a brief derivation of the acoustic plasmon mode in a lattice using a local orbital representation for the dielectric response function of the electrons.[10,11]

II. ACOUSTIC PLASMONS IN MIXED-VALENCE METALS

The mixed-valence problem is a very complicated problem and although the general phenomenological features are mostly agreed upon, a convincing microscopic description is as yet lacking. It is clear, however, that near the Fermi surface, Landau quasiparticles, which are hybridized f and s-d states, exist, and they may be described by Bloch functions as follows:

$$\Psi_{\vec{k}\lambda\sigma}=\sum_{\vec{l}}[A^{f\sigma}_{\vec{k},\lambda}\Phi_{f\sigma}(\vec{r}-\vec{l})+A^{c\sigma}_{\vec{k},\lambda}\Phi_{c\sigma}(\vec{r}-\vec{l})]e^{-i\vec{k}\cdot\vec{l}} \tag{1}$$

where λ is a band index, $\Phi_{f\sigma}$ denotes an f orbital, and $\Phi_{c\sigma}$

denotes the conduction orbitals; $\vec{1}$ are lattice sites which are summed over.

The complicated aspect of the problem is in the calculation of the hybridization coefficients $A_{\vec{k},\lambda}$ and in the quasiparticle normalization at different $\vec{k},\lambda$'s. As long as the material behaves as a two-component Fermi liquid there is probably no very peculiar behavior of these quantities.

At this stage, we recognize that, for simple models of mixed valence, e.g., the case of a single spin-$\frac{1}{2}$ (doublet) f level hybridized with a single conduction band, the hybridization produces a gap and the Fermi level may be trapped either in the gap or in a single heavy-mass band near the gap edge. For such models, the conditions for the existence of acoustic plasmons do not exist,[12,13] since these require both heavy- *and* light-mass regions of the Fermi surface. However, we should recognize that, empirically, transport measurements or de Haas–van Alphen measurements indicate the occurrence of at least some light-mass electrons at the Fermi surface in metals which have mixed-valence or "dense Kondo" behavior.[14–16] These could, for instance, arise from more complicated mixing schemes between degenerate multiplet f levels and complex conduction bands, or from more subtle many-body effects as yet poorly understood. We thus, in this paper, examine the consequences of the occurrence of such a two-component Fermi liquid on the low-lying collective excitation.

With the above quasiparticle basis set, we calculate the density-response function with the random-phase approximation (RPA) modified to exclude double occupancies of f states at a site in an approximate fashion. The RPA is almost certainly not valid in detail, but again just as for an ordinary Fermi liquid, we might expect it to give the correct qualitative features. The density-response function in the RPA is calculated from the matrix

$$\chi_{\mu_1\mu_2}(\vec{q},\omega)=\{[\underline{1}-\underline{\chi}^0(\vec{q},\omega)\underline{\tilde{V}}(\vec{q})]^{-1}\underline{\chi}^0(\vec{q},\omega)\}_{\mu_1\mu_2}\,, \tag{2}$$

where $\mu_1\mu_2$ stand for pairs of orbital indices, ff or cc or fc, and

$$\tilde{V}_{\mu_1\mu_2}(\vec{q})=\sum_{\vec{1}} V_{\mu_1\mu_2}(\vec{1})e^{i\vec{q}\cdot\vec{1}}\,, \tag{3}$$

where $V_{\mu_1\mu_2}(\vec{1})$ is the Coulomb integral between lattice sites a distance $\vec{1}$ apart. For the ff element of (3) the term $\vec{1}=0$ is excluded from the sum. This approximately takes into account that multiple f occupation at a site is strongly disfavored. The bare response $\chi^0_{\mu_1\mu_2}(\vec{q},\omega)$ is

$$\chi^0_{\mu_1\mu_2}(\vec{q},\omega)=\sum_{\vec{k},\lambda_1,\lambda_2}\frac{2(n_{\vec{k},\lambda_1}-n_{\vec{k}+\vec{q},\lambda_2})(E_{\vec{k}+\vec{q},\lambda_1}-E_{\vec{k}+\vec{q},\lambda_2})}{(E_{\vec{k},\lambda_1}-E_{\vec{k}+\vec{q},\lambda_2})^2-\omega^2}A^{\xi_1 *}_{\vec{k},\lambda_1}A^{\xi_2 *}_{\vec{k}+\vec{q},\lambda_2}A^{\xi_4}_{\vec{k}+\vec{q},\lambda_2}A^{\xi_3}_{\vec{k},\lambda_1}\,, \tag{4}$$

where $\mu_1\equiv\xi_1\xi_4$ and $\mu_2\equiv\xi_2\xi_3$. The factor 2 sums over spin indices which are implicitly dropped in (4).

We now focus on the situation peculiar to the mixed-valence compounds where the Fermi level is trapped in a region where the $\Psi_{\kappa\lambda}$ is predominantly f-like in character and where the f-like band has a very large effective mass. The dominant contribution to $\chi^0_{\mu_1\mu_2}$ is then provided when both $\mu_1\mu_2$ are ff, and furthermore by the intraband contribution to it. For frequencies such that

$$\omega \gg \vec{\nabla}E_{\vec{k},\lambda}\cdot\vec{q} \tag{5}$$

for λ in the low-velocity band, we can write, using Eq. (4),

$$\chi^0_f(q,\omega)\simeq\frac{n_f}{m_f^*}\frac{q^2}{\omega^2}\,, \tag{6}$$

where

$$\frac{n_f}{m_f^*}\equiv\frac{\Omega}{4\pi_3}\int dS_{\vec{k}}\,|A^f_{\vec{k},\lambda}|^4(\vec{\nabla}_{k_z}E_{\vec{k},\lambda})^2|\vec{\nabla}_{k_z}E_{\vec{k},\lambda}|^{-1}\,, \tag{7}$$

where Ω is the crystal volume, q is assumed to be along the z axis, and the integral is over the Fermi surface. Now, by block-partitioning the matrix $[\underline{1}-\underline{\chi}^0\underline{\tilde{V}}]$ into parts involving f orbitals and those not involving f orbitals, it may be shown that

$$[(\underline{1}-\underline{\chi}^0\underline{\tilde{V}})^{-1}]_{ff,ff}=\left[1-\frac{n_f}{m_f^*}\frac{q^2}{\omega^2}\tilde{V}^{sc}_{ff,ff}(\vec{q})\right]^{-1}\,, \tag{8}$$

where

$$\tilde{V}^{sc}_{ff,ff}(\vec{q})=\sum_{\vec{1}}V^{sc}_{ff,ff}(\vec{1})e^{i\vec{q}\cdot\vec{1}} \tag{9}$$

and $V^{sc}_{ff,ff}(\vec{1})$ is the Coulomb interaction between f-charge distribution between the site at the origin and at the site $\vec{1}$, but screened by the conduction-orbital components of the screening function $(\underline{1}-\underline{\chi}^0\underline{\tilde{V}})$. This screening is adiabatic because of the assumption

$$\omega \ll E_{\vec{k},\lambda_1}-E_{\vec{k}+\vec{q},\lambda_2}\,, \tag{10}$$

where λ_1,λ_2 refer to conductionlike (high-velocity) bands. [Compare these to one assumption (5).] The simultaneous satisfaction of assumptions (5) and (10) allows the existence of the acoustic plasmon modes.

Equations (2), (6), and (8) give, for the screened f-like part of the density-response function,

$$\chi_f(q,\omega)=\frac{n_f}{m_f^*}\frac{q^2}{(\omega^2-c_p^2q^2)}\,, \tag{11}$$

where

$$c_p^2=\frac{n_f}{m_f}\tilde{V}^{sc}_{ff}(0)\,. \tag{12}$$

If $\bar{V}_{sc}$ is the screened Coulomb interaction between f electrons on nearest-neighbor sites and z is the number of nearest neighbors, then

$$\tilde{V}_{ff}^{sc}(0) \cong z\bar{V}_{sc} . \tag{13}$$

Equations (12) and (13) determine the acoustic plasmon velocity c_p. For the above treatment to be valid, we must self-consistently have

$$v_f \ll c_p \ll v_c , \tag{14}$$

where v_f is the f-electron Fermi velocity and v_c is a typical conduction-electron velocity.

III. COUPLING TO PHONONS

We consider the "bare" phonon frequencies $\tilde{\omega}_{\vec{q},j}$ as the frequencies unrenormalized by the (diagonal) f-like contribution to the density-response function. The coupling of the phonons to the f electrons is predominantly through the local f-electron density[17] and the Hamiltonian may thus be written as

$$H = H_{el} + \sum_{\vec{q},j} \hbar\tilde{\omega}_{\vec{q},j}(b^{\dagger}_{\vec{q},j}b_{\vec{q},j}+\tfrac{1}{2}) + \sum_{\vec{q},j,\alpha}\sum_{\vec{l},\sigma}\left[\frac{\hbar}{2NM\tilde{\omega}_{\vec{q},j}}\right]^{1/2} c^{\dagger}_{\vec{l},\sigma}c_{\vec{l},\sigma}(b_{\vec{q},j}+b^{\dagger}_{-\vec{q},j})e^{i\vec{q}\cdot\vec{l}}P_{\alpha}(\vec{q})e_{\alpha}(\vec{q},j) , \tag{15}$$

where

$$P_{\alpha}(\vec{q}) = \sum_{\vec{l}} F_{\alpha}^{\vec{l}}(e^{i\vec{q}\cdot\vec{l}}-1) , \tag{16}$$

$F_{\alpha}^{\vec{l}}$ being the force which the f-electron density at the origin exerts on the atom at $\vec{l}$. Let us now restrict ourselves to longitudinal modes only. For small q (and $\vec{q}$ and α along a symmetry direction), $P_{\alpha}(\vec{q})$ may be written as iPq.

By considering the case where $F_{\alpha}(l)$ is a radial force coupling only nearest-neighbor atoms to the f-electron density on the origin atom and imagining a uniform dilation of the lattice by a volume increment ΔV, we obtain from the Hamiltonian of Eq. (15), by using mean-field theory, the change in f-electron energy per unit cell,

$$\Delta E = \langle n_f \rangle \frac{P}{3V_0}\Delta V_0 , \tag{17}$$

where V_0 is the unit-cell volume and $\langle n_f \rangle$ is the average f-shell occupation per unit cell. From Eq. (17), we obtain the bare bulk modulus B,

$$B = \frac{P}{3}\frac{\partial \langle n_f \rangle}{\partial V_0} , \tag{18}$$

which serves to evaluate P in terms of experimental quantities. B is renormalized by the coupling to the acoustic plasmon as may be seen by Eq. (22) below.

The equation of motion for the one-phonon Green's function including the f-electron density response yields renormalized phonon frequencies

$$\omega_{q,j}^2 = \tilde{\omega}_{q,j}^2 + \frac{1}{M}P^2q^2\chi_f(q,\omega_{q,j}) . \tag{19}$$

If $\tilde{c}_j$ is the hypothetical velocity of sound for the longitudinal mode in the *absence* of f electrons (but with the Fermi level at the same place in the conduction band),

$$\tilde{\omega}_{\vec{q},j} = \tilde{c}_j q . \tag{20}$$

Thus, by Eqs. (11) and (19),

$$\omega_{q,j}^2 = \tilde{c}_j^2q^2 + \frac{1}{M}P^2\frac{n_f}{m_f^*}\frac{q^4}{(\omega_{q,j}^2 - c_p^2q^2)} . \tag{21}$$

Equation (21) yields solutions

$$\omega_{q,j}^2 = \tfrac{1}{2}\{\tilde{c}_j^2 + c_p^2 \pm [(\tilde{c}_j^2 - c_p^2)^2 + 4D^2]^{1/2}\}q^2 , \tag{22}$$

where

$$D = \frac{1}{M}P^2\frac{n_f}{m_f^*} , \tag{23}$$

which shows the existence of two acoustic branches of mixed-phonon and plasmon character in the long-wavelength limit.

IV. EXPERIMENTAL CONSEQUENCES AND DISCUSSION

It would be interesting to look for the existence of such coupled longitudinal acoustic modes in intermediate-valence metals, perhaps by ultrasonic techniques. We can estimate the velocity of the acoustic plasmon mode for an effective f-electron mass of 100 to be of the order of 10^7 cm/sec, which may make it hard to observe.

From Eq. (22), the longitudinal sound velocity suffers a shift downward and the acoustic plasmon velocity a shift upwards due to their mutual interaction. This effect would be of little importance at larger q and therefore gives rise to the anomalous dispersion curves for longitudinal phonons observed in some mixed-valence compounds.[18]

Qualitatively, the effect we are speaking of here is an effect due to the screening response of the electron system to a phonon mode of long wavelength, but the response is in this case a dynamic one, as opposed to the usual adiabatic screening which is probably valid for considering phonon softening effects at larger values of q. The latter effects can be understood by replacing $\chi_f(q,\omega_{q,j})$ by $\chi_f^s(q)$ [the static limit of Eq. (19) in the case where all the orbitals are f orbitals] in Eq. (19), and replacing P^2q^2 by $-[P_{\alpha}(\vec{q})]^2$. Such a semimicroscopic model can be reproduced through the use of shell models, such as that for the case of the SmS-type compounds.[19] The model used by Entel *et al.*, on the other hand, is rather different, since they parametrize the electron density response (which they also take as nonadiabatic) in terms of a band structure involving a single band hybridized with a flat f level and thus possessing a small hybridization gap. For small q, this model becomes rigorous only for the Fermi level lying in the gap. Thus, for instance, if this is really the case for $Sm_{0.75}Y_{0.25}S$ at the temperatures for which measurements have been made,[18] their model may be more valid for this material than the one given here. On the other hand, the response function used by Entel *et al.* is not the full self-consistent response function (including screening effects), so that if light-mass conduction electrons exist at the Fermi level in this or other mixed-valence or dense Kondo systems (e.g., $CeSn_3$ or $CePd_3$), the dynamic electron response may be important for long-wavelength longitudinal-acoustic modes.

ACKNOWLEDGMENTS

We would like to thank E. I. Blount for a discussion of the requirements imposed by translational invariance in the present problem. The part of this work performed at Argonne National Laboratory was supported by the U.S. Department of Energy.

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