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Theory of the phonons and plasmons in mercury chain compounds

Minette M. Mohan*
Department of Physics, Rutherford Building, McGill University, 3600 University Street, Montreal, Canada H3A 2T8
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A microscopic model is introduced for the density fluctuations in the mercury chains of $Hg_{3-\delta}AsF_6$. Both the one-dimensional phonons measured by neutron scattering experiments, at wave vectors close to a chain lattice vector, and the two-dimensional high-frequency plasmon mode observed in optical reflectance measurements, are recovered. It is predicted that the two phonon modes of the separate sublattices are replaced by a single higher-dimensional phonon mode at wave vectors smaller than the smallest reciprocal-lattice vector, and that a new acoustic plasmon is present.

The first x-ray diffraction[1] experiments on the mercury chain compound $Hg_{3-\delta}AsF_6$ revealed the unusual feature of intense sheets of diffuse scattering in two perpendicular directions. These sheets originate from chains of Hg atoms running through the crystal in "channels" created by the AsF_6 anions and forming two mutually perpendicular arrays of chains a and b. At room temperatures $\simeq 300$ K, the Hg ions are uncorrelated from one chain to the next; thus, each chain acts as an intense one-dimensional (1D) scatterer.[1-3] Further, inelastic neutron scattering experiments[4] at momentum transfers close to $2\pi/d_{\parallel}$, where $d_{\parallel}$ is the Hg intrachain distance, have measured one-dimensional longitudinal acoustic phonons with speed c, associated with the Hg chains. Interactions with the host AsF_6 lattice are weak because[1,5] $d_{\parallel}=(3-\delta)a_T$ where $\delta\simeq 0.18$ and is thus, incommensurate with the host lattice parameter a_T. The striking feature of these compounds, therefore, is that, in contrast to other quasi-1D compounds,[6] both the ions and electrons exhibit 1D characteristics. As the temperature is lowered the two arrays of chains gradually become more correlated, finally ordering to a two-dimensional structure below $T_c\simeq 120$ K.

There are, however, experimental features of these compounds in which the two-dimensional character associated with the two, mutually perpendicular arrays, is apparent, even at room temperature. Optical reflectance measurements[7] on single crystals support a plasmon dispersion relation isotropic in the x-y plane. For light polarized along the z direction, no metalliclike behavior characteristic of freely moving electrons was observed since the crystal remained opaque. For light polarized in the x-y plane, however, the reflectance dropped rapidly at the plasma edge which was found to be $\simeq 4.8\pm 0.3$ eV using a fit to a simple Drude model.

We present a unified microscopic theory of the Hg chains, in which both the one-dimensional character of the phonons and the two-dimensional nature of the plasmons are exhibited. We start with a microscopic model of the room-temperature phase in which the density fluctuations are well represented by plane waves[2,8,9] parallel to the chain axis. Thus, only motion parallel to the chain axis within a given chain is allowed, the density fluctuations being restricted to the chain in the transverse direction.[9] The coupling of the Hg chains to the AsF_6 lattice is ignored,[2] the AsF_6 lattice being treated as a dispersionless background, and retardation is neglected.[10] We show explicitly how the sublattices decouple in response to an external potential $V_0(\mathbf{p}')$ with $\mathbf{p}'$ close to a reciprocal-lattice vector, while in the $\mathbf{p}'\to 0$ limit, the collective modes display the full symmetry of the coupled arrays.

We introduce the microscopic model[9,11] for the density fluctuations,

$$\langle\delta\rho^s(\mathbf{r},\omega)\rangle\equiv\sum_{\mathbf{R}_\perp^s}\delta\rho^s_{\mathbf{R}_\perp^s}(x^s,\omega)w(\mathbf{r}_\perp^s-\tilde{\mathbf{R}}_\perp^s)\ , \tag{1}$$

where $\delta\rho^s_{\mathbf{R}_\perp^s}$ is the density fluctuation on the chain labeled by lattice vector $\mathbf{R}_\perp^s$ of the tetragonal lattice for array s, and $x^a\equiv x$, $x^b\equiv y$. For an origin on the a array, $\tilde{\mathbf{R}}_\perp^b\equiv\mathbf{R}_\perp^b(x,z)+\mathbf{D}^{ab}$; $\mathbf{D}^{ab}\equiv(c_T/4)\hat{\mathbf{z}}+(a_T/4)\hat{\mathbf{x}}$; and $\tilde{\mathbf{R}}_\perp^a\equiv\mathbf{R}_\perp^a(y,z)$. The density fluctuations appearing in Eq. (3) are well represented as a product of plane waves parallel to the chain axis and real-space form factors $w(\mathbf{r}_\perp^s)$ localizing them to the chains in the transverse direction. The $w(\mathbf{r}_\perp^s)$ are taken to be Gaussians[9-11] for simplicity:

$$w(\mathbf{r}_\perp^a)\equiv(\pi r_0^2)^{-1}\exp[-(|\mathbf{r}_\perp^a|/r_0)^2]\equiv w(y)w(z)\ ,$$

and similarly for $w(\mathbf{r}_\perp^b)$, where r_0 is the chain "radius." The self-consistent mean-field equations to be solved for the response functions are thus

$$\langle\delta\rho^a(\mathbf{r},\omega)\rangle=\sum_s\int d\mathbf{r}'\sum_{\mathbf{R}_\perp^a}\chi^{0a,a}(x,x',\omega)w(\mathbf{r}_\perp^a-\mathbf{R}_\perp^a)w(\mathbf{r}_\perp'^a-\mathbf{R}_\perp^a)V^a_{\rm tot}(\mathbf{r}',\omega)\ , \tag{2}$$

and

$$V^a_{\rm tot}(\mathbf{r}',\omega)=V_0^a(\mathbf{r}',\omega)+\sum_s\int d\mathbf{r}''v^{a,s}(|\mathbf{r}'-\mathbf{r}''|)\langle\delta\rho^s(\mathbf{r}'',\omega)\rangle\ , \tag{3}$$

where $\chi^{0a,a}_{\mathbf{R}^a_\perp,0}(x,x',\omega)\equiv\chi^{0a,a}(x-x',\omega)$, independent of $\mathbf{R}^a_\perp$, is the one-dimensional Lindhard function.[12] $v^{a,s}(r)=e^2/r$ is the interaction potential energy between density fluctuations.

The general response function in the model is

$$\bar{\chi}^{a,s}(\mathbf{p},-\mathbf{q},\omega)\equiv\beta(\mathbf{p}^a_\perp)\beta^*(\mathbf{q}^s_\perp)\frac{1}{N}\sum_{\mathbf{R}^a_\perp,\mathbf{R}^s_\perp}e^{i\mathbf{p}\cdot\mathbf{R}^a_\perp}\chi^{a,s}_{\mathbf{R}^a_\perp-\mathbf{R}^s_\perp}(p_x,-q^s_x,\omega)e^{-i\mathbf{q}\cdot\tilde{\mathbf{R}}^s_\perp}\ , \tag{4}$$

where N is the number of chains in each array, assumed equal, and $\beta(\mathbf{p}^s_\perp)$ are the Fourier transforms of the Gaussians $w(\mathbf{r}^s_\perp)$. The functions $\bar{\chi}^{a,s}(\mathbf{p},-\mathbf{q},\omega)$ are the Fourier transforms of $\chi^{a,s}(\mathbf{r},\mathbf{r}',\omega)$ and automatically satisfy the translational symmetry in real space $\chi^{s,s}(\mathbf{r},\mathbf{r}')=\chi^{s,s}(\mathbf{r}+\mathbf{R}^s_\perp,\mathbf{r}'+\mathbf{R}^s_\perp)$, and $\chi^{s,s'}(\mathbf{r},\mathbf{r}')=\chi^{s,s'}(\mathbf{r}+\mathbf{R}^s_\perp,\mathbf{r}'+\mathbf{R}^s_\perp)=\chi^{s,s'}(\mathbf{r}+\mathbf{R}^{s'}_\perp,\mathbf{r}'+\mathbf{R}^{s'}_\perp)$.

Using the above, we obtain a set of coupled equations which can be solved to give the response functions. The analysis makes use of the restriction of the dynamics of the problem to motion only along the chain axis within a given chain. We obtain

$$\begin{aligned}\chi^{a,a}(\mathbf{p},-\mathbf{p}-\mathbf{G}^a_\perp,\omega)&=\frac{\chi^{0a,a}(\mathbf{p},-\mathbf{p}-\mathbf{G}^a_\perp,\omega)\epsilon^b(\mathbf{p},\omega)}{\det\epsilon(\mathbf{p},\mathbf{G}^a_\perp,\omega)}\ ,\\ \chi^{a,b}(\mathbf{p},-\mathbf{p}-\mathbf{G}^b_\perp,\omega)\delta_{\mathbf{G}^b_\perp,\mathbf{G}^a_\perp}&=\frac{|\beta(p_y)|^2\chi^{0a,a}(p_x,-p_x,\omega)u^{a,b}(\mathbf{p})\chi^{0b,b}(\mathbf{p},-\mathbf{p}-\mathbf{G}^b_\perp,\omega)}{\det\epsilon(\mathbf{p},\mathbf{G}^a_\perp,\omega)}\ ,\end{aligned} \tag{5}$$

and similarly for $\chi^{b,b}$ and $\chi^{a,a}$, where

$$\det\epsilon(\mathbf{p},\mathbf{G}^a_\perp,\omega)\equiv\epsilon^a(\mathbf{p},\omega)\epsilon^b(\mathbf{p},\omega)-|\beta(p_{xy})|^2\chi^{0a,a}(p_x,-p_x,\omega)u^{a,b}(\mathbf{p})\chi^{0b,b}(p_y,-p_y,\omega)u^{b,a}(\mathbf{p})\delta_{\mathbf{G}^a_\perp,\mathbf{G}^b_\perp}\ , \tag{6}$$

$$\epsilon^s(\mathbf{p},\omega)\equiv 1-u^{s,s}(\mathbf{p},\omega)\chi^{0s,s}(p^s_x,-p^s_x,\omega)\ . \tag{7}$$

The wave number $p_{xy}\equiv(p_x^2+p_y^2)^{1/2}$ and the form-factored Coulomb potential energies $u^{s,s}(\mathbf{p})$ are given by

$$u^{s,s}(\mathbf{p})\equiv\sum_{\mathbf{G}^s_\perp}|\beta(\mathbf{p}^s_\perp+\mathbf{G}^s_\perp)|^2 v(\mathbf{p}+\mathbf{G}^s_\perp)\ , \tag{8a}$$

$$u^{s,s'}(\mathbf{p})\equiv\sum_{\mathbf{G}^s_\perp}|\beta(\mathbf{p}^s_\perp+\mathbf{G}^s_\perp)|^2 v(\mathbf{p}+\mathbf{G}^s_\perp)e^{i\mathbf{G}^s_\perp\cdot\mathbf{D}_{ab}}\delta_{\mathbf{G}^s_\perp,\mathbf{G}^{s'}_\perp}\ . \tag{8b}$$

where $v(\mathbf{p})\equiv 4\pi e^2\eta L/p^2$ and η is the number of electrons per unit volume in one array.

Thus we have

$$\begin{aligned}\langle\delta\rho^a(\mathbf{p},\omega)\rangle=&\sum_{\mathbf{G}^a_\perp}\chi^{a,a}(\mathbf{p},-\mathbf{p}-\mathbf{G}^a_\perp,\omega)V^a_0(\mathbf{p}+\mathbf{G}^a_\perp)\\ &+\sum_{\mathbf{G}^b_\perp}\chi^{a,b}(\mathbf{p},-\mathbf{p}-\mathbf{G}^b_\perp,\omega)\delta_{\mathbf{G}^b_\perp,\mathbf{G}^a_\perp}V^b_0(\mathbf{p}+\mathbf{G}^b_\perp)\ ,\end{aligned} \tag{9}$$

where $\chi^{a,a}$ and $\chi^{a,b}$ are given by Eqs. (5)–(8). We consider the response to a local[10] (in momentum space) external field,

$$V_0(\mathbf{p}',\omega)=V_0(\mathbf{p},\omega)\delta_{\mathbf{p}',\mathbf{p}+\mathbf{G}^{0,a}_\perp}\ . \tag{10}$$

Therefore, if $\mathbf{G}^{0,a}_\perp=\mathbf{G}^{0,a}_\perp(\hat{\mathbf{z}})\neq 0$ then the b array also responds at some $\mathbf{G}^{0,b}_\perp=\mathbf{G}^{0,a}_\perp$ and the motion is that of the coupled arrays. If, however, $\mathbf{G}^{0,a}_\perp$ has some nonzero y component, it is clear that the response of the two sublattices is completely decoupled and the system behaves as though only the a array were present. The same argument holds if $\mathbf{G}^{0,a}_\perp$ is replaced by $\mathbf{G}^{0,b}_\perp$ with nonzero x component, in which case the response is that of the b array alone. The motion is also coupled in the limit of $\mathbf{p}'\to 0$ which corresponds to the case $\mathbf{G}^{0,a}_\perp=\mathbf{G}^{0,b}_\perp=0$. Finally, the a-b form-factored potential energy in Eq. (8b) can be written as

$$u^{a,b}(\mathbf{p})=\frac{2\pi e^2}{p_{xy}a_T}e^{(p_{xy}r_0)^2/2}\frac{\mathrm{csch}(p_{xy}D)\sec(p_zD)}{1+\tan^2(p_zD)\coth^2(p_{xy}D)}\ , \tag{11}$$

where $D=c_T/4$ is the minimum distance between the a and b arrays in the z direction. This shows the relative restriction of the density fluctuations in the combined a-b system only along the z direction. In this form "corrections" to the continuum $1/p^2$ term are easily obtained.

The collective modes of the system are given by the solutions of the equation $\det\epsilon(\mathbf{p},\omega)=0$. In the continuum limit $pr_0\ll 1$ Eqs. (8) become ($\pi a^2=A_c$, the area of a unit cell of one array)

$$\begin{aligned}u^{s,s}(\mathbf{p})&\simeq\frac{4\pi e^2\eta L}{p^2}[1+(pa)^2C(p^s_x/p)+O(pa)^4]\ ,\\ u^{a,b}(\mathbf{p})&\simeq\frac{4\pi e^2\eta L}{p^2}[1+\tfrac{1}{2}(pD)^2B(\theta)+\tfrac{1}{2}(pr_0)^2\sin^2\theta]\ ,\end{aligned} \tag{12}$$

where the corrections to the usual $1/p^2$ term in the last equation are obtained from the convenient form of Eq. (11). In Eq. (12),

$$C\left(\frac{p^s_x}{p}\right)=\frac{1}{4}\left[\ln\left(\frac{a^2}{2r_0^2}\right)+\gamma-1+2\left(\frac{r_0}{a}\right)^2\left(\frac{p^s_x}{p}\right)^2\right]\ , \tag{13}$$

and

$$B(\theta)=-\tfrac{1}{6}(1+4\sin^2\theta)\ . \tag{14}$$

The angles θ,ϕ are defined by $\mathbf{p}=p(\sin\theta\cos\phi,\ \sin\theta\sin\phi,$

$\cos\theta$), and $\gamma \simeq 0.577$. The single-chain electronic response functions are given in both the high-frequency ($\omega \gg p_x v_F, p_y v_F$) and low-frequency limits ($\omega \ll p_x v_F$, $p_y v_F$) by

$$\chi^{0s,s}(p_x^s, -p_x^s, \omega) \simeq \frac{N_e p_x^{s2}}{m(\omega^2 - v_F^2 p_x^{s2})} , \tag{15}$$

for N_e electrons (mass m) per unit length on a chain, and v_F is the Fermi velocity for electrons on both a and b chains. From Eqs. (12)–(15), the high-frequency collective modes (plasmons) in the $p \rightarrow 0$ limit have frequencies given by

$$\omega_+^2 = \omega_p^2 \sin^2\theta \{1 + (pa)^2 [f(\theta,\phi) - \tfrac{1}{4}\sin^2 2\phi\, g(\theta,\phi)]\} + v_F^2 p^2 \sin^2\theta (1 - \tfrac{1}{2}\sin^2 2\phi) , \tag{16}$$

and

$$\omega_-^2 = \tfrac{1}{2} v_F^2 p^2 \sin^2\theta \sin^2 2\phi [1 + \alpha(\theta)] , \tag{17}$$

involving the joint motion of both sublattices. Here, $\omega_p^2 = 4\pi N N_e e^2/m$ is the Drude plasma frequency and

$$f(\theta,\phi) = \frac{1}{4}\left[\ln\left(\frac{a^2}{2r_0^2}\right) + \gamma - 1 + 2\left(\frac{r_0}{a}\right)^2 \sin^2\theta (1 - \tfrac{1}{2}\sin^2 2\phi)\right] ,$$

$$g(\theta) = \frac{1}{2}\left[\ln\left(\frac{a^2}{2r_0^2}\right) + \gamma - 1 + \frac{2}{3}\left(\frac{D}{a}\right)^2 (1 + 4\sin^2\theta)\right] ,$$

$$\alpha(\theta) = \frac{\omega_p^2 g(\theta)}{2(v_F a^{-1})^2} . \tag{18}$$

The high-frequency mode ω_+ corresponds to an approximately in-phase motion of the correlated electrons on a and b chains, while the low-frequency acoustic mode ω_- corresponds to a "softer" correlated motion in which the charge-density fluctuations on a and b chains are approximately out of phase. The mode ω_+ has been observed experimentally in optical reflectance measurements. The new acoustic plasmon ω_- which we predict could be observed by fast electron scattering experiments. It should be noted that the nonzero $\alpha(\theta)$ in the dispersion relation of ω_- makes Landau damping[12] of this mode less likely, the conditions $\omega > p_x v_F, p_y v_F$ also restricting propagation of this mode to a small angular region in the $x-y$ plane in the vicinity of $\pm\phi = \pi/4, 3\pi/4$.

The generalization of Eq. (6) to include the ions (charge Z, mass M) in the chains gives in the $p' \rightarrow 0$ limit where $\mathbf{p}'$ is the wave vector of Eq. (10).

$$\det \epsilon'(\mathbf{p},\omega) = 1 - \frac{4\pi e^2 \eta L}{p^2} \sum_s [\chi_{e,e}^{0s,s}(p_x^s, -p_x^s, \omega) + Z^2 \chi_{I,I}^{0s,s}(p_x^s, -p_x^s, \omega)] = 0 , \tag{19}$$

on keeping only the $1/p^2$ terms in Eq. (22). The solutions of this equation in the "phonon regime" (Refs. 9 and 13) $v_I \ll c \ll v_F$ where v_I is a typical ionic velocity in the chain, are the phonon modes given by $\omega = c_{2d}(p_x^2 + p_y^2)^{1/2}$, where $c_{2d} \equiv [(Zm)/(2M)]^{1/2} v_F$ is the Bohm-Staver velocity in two dimensions $c_{2d} \ll v_F$. The phonon regime corresponds to electronic screening of the ionic charge to a short-ranged potential necessary for sound waves. Thus, in the "true" long wavelength limit $p' \rightarrow 0$ the a and b sublattices exhibit coupled-mode behavior in both the high- and low-frequency regimes. The AsF_6 lattice also supports phonons,[14] however, we expect that the longitudinal modes of this lattice would be mixed in with the pure Hg mode. Thus, one would observe a 3D anisotropic dispersion relation for the phonons, even at room temperature.

In contrast, at wave vectors $\mathbf{p}'$ of Eq. (10) close to

$$\mathbf{G}_{ch}^{a(b)} = \hat{\mathbf{x}}(\hat{\mathbf{y}}) 2\pi n/[d_\parallel = (3-\delta)a_T] ,$$

the Hg chain phonons have been measured by neutron scattering experiments.[4] In this case, the phonons are the solutions to the uncoupled equations[15] ($p \rightarrow 0$)

$$\det(\epsilon^s)' = 1 - \frac{4\pi e^2 \eta L}{p^2} [Z^2 \chi_{I,I}^{0s,s}(p_x^s, -p_x^s, \omega) + \chi_{e,e}^{0s,s}(p_x^s, -p_x^s, \omega)] = 0 . \tag{20}$$

In this case, the modes are given by

$$\omega = c_{1D} p_x, \text{ or } \omega = c_{1D} p_y , \tag{21}$$

where c_{1D}, the Bohm-Staver velocity in one dimension, is the single chain phonon velocity,[9] $\simeq 3\times 10^2$ ms^{-1} in reasonable agreement with the value $(4.4 \pm 0.8)\times 10^2$ ms^{-1}. A more complete theory would incorporate the AsF_6 lattice phonons, but it should be clear that the formalism presented above can be generalized to any number of interpenetrating incommensurate lattices. At larger wave vectors the modes would be those of the three *separate* lattices since there are no nonzero lattice vectors in common. In this case, there are none in common in the x-y plane and no Hg motion is possible along the z direction, hence, the modes of all three sublattices would be uncoupled.

To summarize, we have presented a microscopic model for the density fluctuations on the Hg chains which quantitatively reproduces the experimentally observed room-temperature collective modes. At wave vectors close to an arbitrary reciprocal-lattice vector, the two arrays decouple, and the modes are 1D. The dispersion relation for the Hg chain phonons at wave vectors close to $2\pi/d_\parallel$ are shown to be in agreement with neutron inelastic measurements. These phonons have speed c_{1D}, the Bohm-Staver velocity in one dimension, roughly in agreement with the measured sound velocity.[16] In the special case where the external probe has wave vector smaller than any lattice vector in the system, a single 3D anisotropic phonon mode is predicted. The dispersion relation for the plasmons is calculated and exhibits 2D behavior in agreement with the optical reflectance experiments. A new 2D acoustic plasmon associated with out of phase vibration of the joint arrays, is found.

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*Present address: Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K2R1.

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[15]Phonon damping, which is ignored here, is expected to be more important however for $p_x' = p_y'$, in which case one might expect a coupled-mode solution (see also Refs. 2 and 14).

[16]In the "point ion" approximation, which we have used, the core-core repulsion of the closed shells of electrons has been neglected and this effect should act to increase the sound velocity, in analogy with bulk metals, by roughly 10%.