Theory of the Crossover in the Low-Frequency Dynamics of an Incommensurate System, $Hg_{3-\delta}AsF_6$

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The dynamic structure factor of a three-dimensional crystal, with an interpenetrating set of atomic chains which form one-dimensional fluids, is studied. At high frequencies there are two longitudinal acoustic modes arising from the separate motion of the lattice and fluid. At low frequencies there is one combined propagating longitudinal acoustic mode and a diffusive excitation due to particle motion. The crossover between these regions is predicted to occur at a frequency ~ MHz in $Hg_{3-\delta}AsF_6$.

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In this Letter we study the dynamical modes of a three-dimensional (3D) crystal with an interpenetrating set of atomic chains which form one-dimensional fluids. $Hg_{3-\delta}AsF_6$ at $T > 120$ K is such a compound with a body-centered-tetragonal (bct) AsF_6 lattice and nonintersecting Hg chains in the ab planes.[1] A neutron investigation[2] found two propagating longitudinal acoustic (LA) modes with different velocities associated with the separate motion of the Hg chains and the AsF_6 lattice down to the lowest attainable frequency (~ 10 GHz). This raises an interesting question since in the true long-wavelength limit one expects only one propagating LA mode associated with a combined motion of the $Hg_{3-\delta}AsF_6$ sample. The question then, which has not been dealt with previously, is how the two separate LA modes evolve at lower frequencies to give a single combined LA mode.

The Hg chains form strongly correlated 1-D fluids with an average nearest-neighbor separation (2.67 Å) which is incommensurate with the lattice parameter of the AsF_6 lattice (7.53 Å). This leads to a very weak coupling of the motion of the Hg atoms along the chains and the AsF_6 lattice. The structure factor $S(q,\omega)$ is defined as[3]

$$S(q,\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle \rho(-q,t)\rho(q,0)\rangle \qquad (1)$$

with the density operator

$$\rho(q,t) = \exp(iLt)\sum_{i,\mu} \exp(-iqX_{\mu i}).$$

L denotes the Liouville operator and the vector q lies along a chain direction, $\hat{x}$. The sum i runs, for $\mu = a$, over all Hg sites which pertain to chains along the x direction and, for $\mu = b$, over the remaining AsF_6 and Hg positions. If we ignore for the moment the interaction between the a and b subsystems then S decomposes into two parts; the b part has the usual form for a 3-D lattice, while the a part has the form[3]

$$S_a(q,\omega) = \frac{-2N_a k_B T q^2 \Pi_a^{(2)}(q,\omega)/m_a}{[\omega^2 - \Omega_a^2(q) - \omega\Pi_a^{(1)}(q,\omega)]^2 + [\omega\Pi_a^{(2)}(q,\omega)]^2}, \qquad (2)$$

where the self-energy $\Pi \equiv \Pi^{(1)} + i\Pi^{(2)}$, and N_a and m_a are the number and mass of the a ions. Ω_a^2/q^2 is proportional to the inverse of the static structure factor and in the limit $q \to 0$ determines the sound velocity of the a chains, v_a^4, while $\Pi_a(q,\omega) = -i\gamma_a q^2$ as $(q,\omega) \to 0$. The existence of a well-defined propagating mode at long wavelengths is a consequence of the conservation of the total momentum of the a chains.[3] In this form S has two propagating LA modes in the whole frequency range.

We now consider the effect of the coupling between the a and b subsystems. Because of the incommensurability there is no overlap along the x direction between the positions of the quasi-Bragg peaks of the a chains and the reciprocal lattice vectors of the b lattice, G_b. However, we find that there are other coupling mechanisms. It is convenient to introduce a matrix notation and

write

$$S(q,\omega)=2k_B T\,\mathrm{Im}\sum_{\mu,\nu}\chi_{\mu,\nu}(q,\omega)/\omega, \quad (3)$$

where the indices (μ,ν) take the values a and b and the response matrix χ satisfies[3]

$$\chi(q,\omega)=-q^2 m^{-1}[\omega^2-\Omega^2(q)-\omega\Pi(q,\omega)]^{-1}N, \quad (4)$$

with the matrices

$$N=\begin{pmatrix} N_a & 0 \\ 0 & N_b \end{pmatrix}, \quad m^{-1}=\begin{pmatrix} m_a^{-1} & 0 \\ 0 & m_b^{-1} \end{pmatrix}, \quad (5)$$

and $N_b=M_b m_b^{-1}$. M_b denotes the total mass of subsystem b while m_b is an effective ionic mass related to the in-phase motion of the AsF_6 ions with ionic mass m_1 and total mass M_1 and the Hg ions of the b subsystem with total mass M_a, $m_b^{-1}=(m_1^{-1}M_1+m_a^{-1}M_a)/M_b$. The frequency matrix $\Omega^2(q)$ is related by (4) to the inverse static susceptibility matrix $\chi^{-1}(q)$. To avoid unnecessary complications we neglect the off-diagonal terms in $\chi^{-1}(q)$, and as $q\to 0$,

$$\Omega_{\mu\mu}^2(q)=v_\mu^2 q^2=N_\mu\chi_{\mu\mu}^{-1}(q=0)m_\mu^{-1}q^2. \quad (6)$$

The only effect of these off-diagonal terms, which are proportional to q^2, is to change slightly the sound velocities and they can be safely neglected for the case of $Hg_{3-\delta}AsF_6$.[4]

The intersystem interaction gives a finite contribution to Π as $(q,\omega)\to 0$ in contrast to the vanishing terms from intrasystem interactions as discussed above. We can represent then

$$\Pi(q=0,\omega\to 0)=\begin{pmatrix} -M_b & M_a \\ M_b & -M_a \end{pmatrix}M^{-1}i\gamma, \quad (7)$$

with $M_\mu=N_\mu m_\mu$ and $M=M_a+M_b$. The self-energy γ can be calculated by examining the force equation for each subsystem in the presence of intersystem interactions. The nonzero terms come from two sources. One is due to the direct overlap of the static structure factors of the two systems. Such an overlap arises here because of the fluid character of the a chains which gives a small but finite value for $S_a(q=G_b,0)$. A much larger term (by a factor ~10) arises from a dynamic resonance process. The existence of points of degeneracy in both energy and momentum of the modes of the a and b subsystems allows the interchange of energy and momentum in the long-wavelength limit between the subsystems. It gives a form

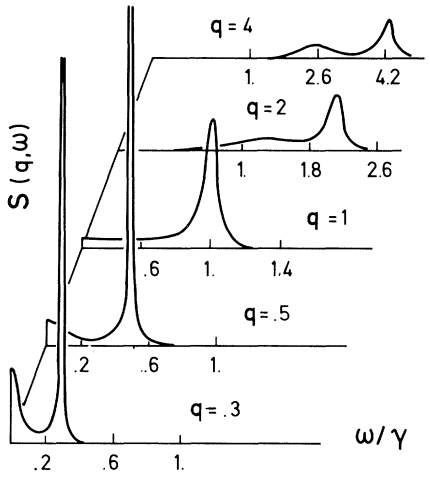

FIG. 1. The calculated dynamic structure factor $S(q,\omega)$. At frequencies $\omega\gtrsim\gamma$ the two peaks are due to the separate LA modes of the Hg chains (upper) and AsF_6 lattice (lower). At low frequencies the peak at finite ω is from the combined LA mode and the central peak from the particle diffusion mode. The third mode due to the relaxation of relative linear momentum has very little weight in $S(q,\omega)$ at small q. The wave vector q is given in units γ/v_s.

$$\gamma=\frac{Mk_B T}{M_a M_b}\sum_\alpha d^3k|V_\alpha(k)|^2 k_x^4\Omega_a^{-4}(k_x)\delta[\Omega_{b\alpha}(\vec{k})-\Omega_a(k_x)], \quad (8)$$

where the sum α runs over the modes of subsystem b with frequencies $\Omega_{b\alpha}(\vec{k})$ while $V_\alpha(\vec{k})$ is related to the potential generated by these modes along the a chains. This potential originates from the Coulomb interaction between the ions.[4,5] A detailed discussion will be given in a subsequent paper. Using this potential and the measured values[2] for Ω_μ we obtain an estimated value $\gamma\simeq 1.4$ MHz.[6] In the limit $(q,\omega)\to 0$ we obtain

$$S(q,\omega)=\frac{2k_B T N_a N_b}{M m_a m_b}\,\frac{\gamma q^2[(m_b-m_a)\omega^2+m_a v_a^2 q^2-m_b v_b^2 q^2]^2}{(\omega^2-v_a^2q^2)^2(\omega^2-v_b^2q^2)^2+(\omega^2-v_s^2q^2)^2\omega^2\gamma^2}, \quad (9)$$

where $v_s^2=(M_a/M)v_a^2+(M_b/M)v_b^2$. In Fig. 1 we plot $S(q,\omega)$.

At low frequencies $(\omega\ll\gamma)$ there are three modes. One is a propagating combined sound mode with velocity v_s and a damping $\propto q^2$. The second mode is a particle diffusion mode[7] with $\omega_d=-iq^2v_a^2v_b^2/v_s^2\gamma$.[8] A third mode is a purely relaxational mode with $\omega_r=-i\gamma+O(q^2)$, which is due to the relaxation

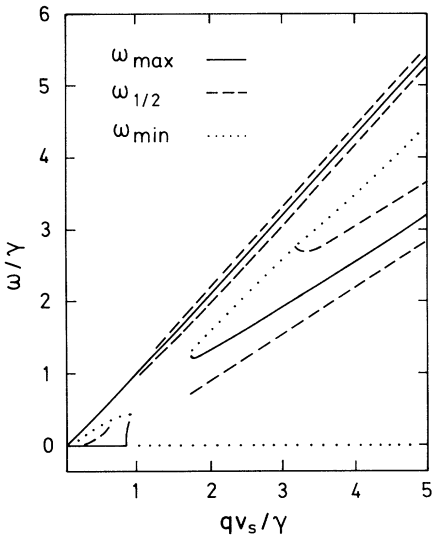

FIG. 2. A contour plot of $S(q,\omega)$ showing the behavior in the crossover regime. The peak due to the lower LA mode terminates at $\omega \simeq 1.2\gamma$. The higher LA mode continues to be well defined at all frequencies but its velocity changes from v_a at high frequencies to v_s—the combined sound-wave velocity. The structure at $\omega < v_s q$ as $(q,\omega) \to 0$ is due to the particle diffusion mode.

of the relative linear momentum of the subsystems.

As the frequency is raised the sound mode continues to be well defined and evolves into the higher sound mode with $\omega = v_a q$. The two relaxational modes disappear and a new sound mode with $\omega = v_b q$ appears for $\omega > \gamma$. In Fig. 2 we give a contour plot of $S(q,\omega)$, showing the maxima, half maxima, and minima associated with the various modes. At still higher frequencies the two sound modes continue to be well defined although the intrinisc linewidths become larger (i.e., $\gamma_a q^2 > \gamma$ for $v_a q \gtrsim 1$ GHz).

Another possible source of coupling is through impurities. We have made calculations for the case where the impurity-induced coupling dominates and find that in that case the modes evolve differently. The lower sound mode joins on to the combined sound mode and the upper sound mode evolves to a pinning frequency for the relative motion of the two systems. In $Hg_{3-\delta}AsF_6$ experiments show that the correlation length of the Hg chains at room temperature is determined by intrinsic thermal fluctuations[2,9] and in this case we find that the intrinsic coupling discussed above dominates.

In conclusion we have examined the low-frequency modes of a 1D fluid interpenetrating a 3D lattice. We predict a crossover at low frequencies from two propagating LA modes to one combined sound mode and two relaxational modes. Experiments to test the predictions of our theory would be most welcome.

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[3]See, e.g., D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, Reading, Mass., 1975).

[4]V. J. Emery and J. D. Axe, Phys. Rev. Lett. 40, 1507 (1978).

[5]Because of the metallic character of the Hg chains the long-range part of the Coulomb interaction between the a and b subsystems is screened out and the theory of G. Theodorou [Solid State Commun. 33, 561 (1980)] for ionic materials is not applicable here.

[6]This estimate was obtained for a Coulomb interaction with charges $e(AsF_6) = -e$ and $e(Hg) = 1/(3-\delta)e$, the mean charge per Hg. A more accurate calculation has to include the precise form of the screening by conduction electrons of the bare ionic charges, $-e$ and $+2e$, respectively.

[7]This behavior differs from that found in ionic conductors where the long-range part of the Coulomb force gives a finite width for ω_d as $q \to 0$. [R. Zeyher, Z. Phys. B 31, 127 (1978)].

[8]This pole originates from the fact that, since the relative linear momentum of systems a and b is not conserved, the relative displacement mode will be purely diffusive in the hydrodynamic region. [R. Zeyher and W. Finger (to be published)].

[9]R. Spal, C.-E. Chen, T. Egami, P. J. Nigrey, and A. J. Heeger, Phys. Rev. B 21, 3110 (1980).