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Inertial charge-density-wave dynamics in $(TaSe_4)_2I$

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Frequency-dependent conductivity measurements are reported in the charge-density-wave (CDW) state of the linear-chain compound $(TaSe_4)_2I$ in the spectral range 4.5–94 GHz. In contrast to other CDW systems which are overdamped, the response is underdamped, with a resonant frequency of approximately 35 GHz, a resonance width of approximately 20 GHz, and an effective mass of 10^4. The large effective mass, large resonant frequency, and small damping are a consequence of the strong electron-phonon coupling in this system.

The strongly frequency-dependent response observed in several inorganic linear chain compounds in their charge-density-wave (CDW) state is due to the collective response of the pinned condensate.[1] Experiments performed in the model compounds $NbSe_3$ and o-TaS_3 in the radio-frequency spectral range[1] are interpreted either in terms of an overdamped classical response[2] or in terms of ac-field-induced tunneling across a small pinning gap.[3] In this range the conductivity increases with increasing frequencies and tends to saturate at a value which is close to that observed above the phase transition. Due to the limited frequency range, the frequency-dependent response has not been fully characterized, and only some of the parameters have been evaluated. In terms of the classical description,[2] the initial rise of the real part of the conductivity, $\mathrm{Re}\sigma(\omega)$ leads to a so-called crossover frequency $\omega_0^2\tau$. For the tunneling model,[3] $\sigma(\omega)\simeq\exp(-\omega_g/\omega)$, where ω_g is a scaling frequency, and consequently this parameter may be evaluated. The saturation at high radio frequencies is described by the standard expression

$$\sigma_b=\frac{n_{\mathrm{CDW}}e^2\tau}{m^*} \quad , \tag{1}$$

where n_{CDW} is the number of condensed electrons and τ and m^* are the damping constant and effective mass of the condensate. With n_{CDW} known from the band filling, the combination τ/m^*, but not the individual parameters, may be evaluated.

Recent experiments[4] in the millimeter-wave spectral range in $NbSe_3$ and in orthorhombic TaS_3 (o-TaS_3) provide clear evidence for the inertial effects—$\mathrm{Re}\sigma(\omega)$ decreases with increasing frequencies, and $\mathrm{Im}\sigma(\omega)$ is negative. The complex conductivity may be described by a Drude-type expression

$$\sigma(\omega)=\frac{n_{\mathrm{CDW}}e^2\tau}{m^*}\frac{1}{1+i\omega\tau} \quad . \tag{2}$$

This description is possible because in these materials the CDW is overdamped and hence the "relaxational" and "inertial" responses are well separated in frequency. The frequency dependence allows τ to be evaluated, which, with the maximum conductivity, leads to the effective mass m^*. The values for m^* are in good overall agreement with the effective-mass expression which follows from the Lee-Rice-Anderson theory[5] of CDW dyanmics

$$\frac{m^*}{m_b}=1+\frac{4\Delta^2}{\lambda\hbar^2\omega_{2k_F}^2} \quad , \tag{3}$$

where λ is the electron-phonon coupling constant, 2Δ is the single particle gap, ω_{2k_F} is the phonon frequency at $2k_F$, and m_b is the band mass. In the mean field, for weak coupling,

$$\Delta=2\epsilon_F\exp(-1/\lambda) \quad , \tag{4}$$

where ϵ_F is the Fermi energy. Δ may be estimated from the temperature-dependent dc conductivity between the phase transitions, and $\epsilon_F\simeq 0.3$ eV in these materials.[1] The measured values of m^* are in agreement with estimations based on Eqs. (3) and (4), also assuming $\hbar\omega_{2k_F}/k_b=50$ K.

In this Rapid Communication we report frequency-dependent conductivity experiments in the millimeter-wave spectral range in the linear chain compound $(TaSe_4)_2I$. The material undergoes a Peirls transition at 265 K to an incommensurate CDW state, as evidenced by structural studies and by an anomaly in the dc conductivity.[6] The conductivity is not truly metallic above the phase transition; this has been interpreted as resulting from CDW fluctuations.[7] In the CDW state the conductivity is nonlinear above a threshold field E_T, which is larger than in $NbSe_3$ and in TaS_3, with well-defined current oscillations in the nonlinear conductivity region. The conductivity is also frequency dependent and the low-frequency dielectric constant is large,[8] although the ω-dependent response at radio frequencies is weaker than in other materials. The above features are a clear signature of the dynamical response of the collective mode. The experiments in the micrometer- and millimeter-wave spectral ranges were performed using cavity-perturbation (4.5, 9, and 35 GHz) and millimeter-wave bridge (30, 60, and 94 GHz) experimental techniques, as described elsewhere.[9] The $(TaSe_4)_2I$ samples were prepared by the gradient furnace technique; the measured transition temperature and threshold field indicate that the sample quality is comparable with that reported in the literature.

In Fig. 1 the temperature dependence of the conductivity measured at dc and at various frequencies is displayed. A strong dispersion is found below T_p, and the size of the separation between the conductivities indicates a large frequency dependence in the spectral range investigated. In contrast to that observed in $NbSe_3$ and in o-TaS_3, σ (9 GHz) is small, indicating a shift of the spectral weight to higher frequencies than observed in the other two model compounds. This is more clearly demonstrated in Fig. 2, where the frequency dependence of the conductivity measured at $T=150$ K is displayed. The overall behavior indicates a weakly damped response with a quality factor Q of

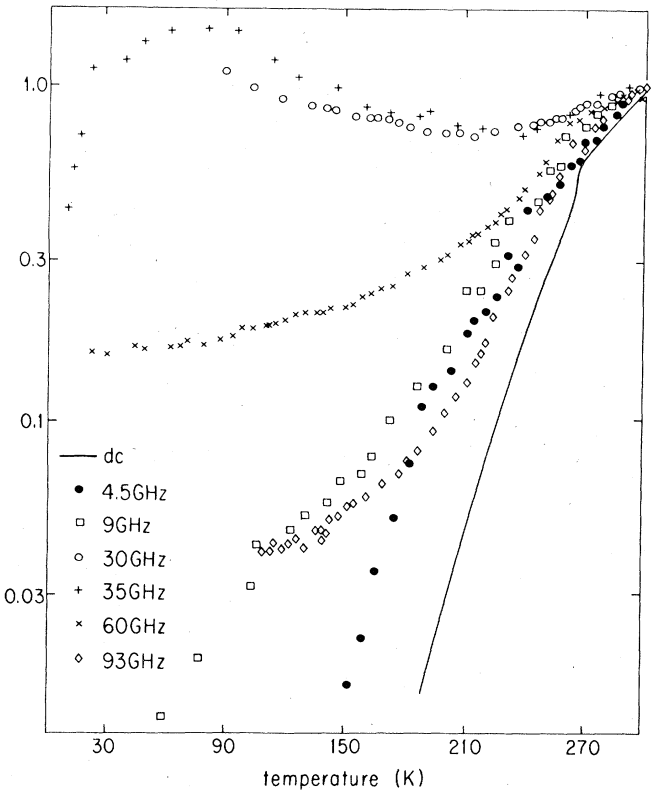

FIG. 1. Log_{10} conductivity vs temperature for $(TaSe_4)_2I$ at various frequencies. The phase transition at $T=265$ K is evidenced by the kink in the dc conductivity curve.

approximately 1 and a resonance frequency of approximately 35 GHz. We have fit the measured conductivity to the classical harmonic-oscillator response

$$\frac{d^2x}{dt^2}+\frac{1}{\tau}\frac{dx}{dt}+\omega_0^2 x=\frac{eE}{m^*}\ , \tag{5}$$

which leads to

$$\mathrm{Re}\sigma(\omega)=\sigma_b\frac{\omega^2/\tau^2}{(\omega^2-\omega_0^2)^2+\omega^2/\tau^2}\ . \tag{6}$$

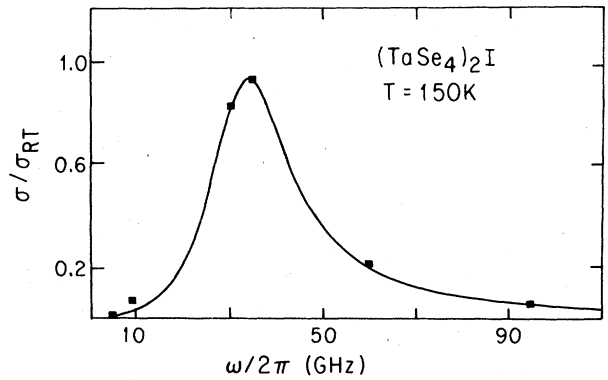

FIG. 2. σ/σ_{RT} vs frequency for $(TaSe_4)_2I$ at 150 K. The solid curve is the best fit to Eq. (6) with $\omega_0/2\pi=34$ GHz, $1/2\pi\tau=21$ GHz, and $\sigma_b=0.93\sigma_{RT}$. σ_{RT} refers to the dc conductivity at room temperature, 350 $(\Omega\ \mathrm{cm})^{-1}$ (Ref. 8).

Equation (6), with parameters $\sigma_b=0.93\sigma_{RT}$, where σ_{RT} is the dc conductivity at room temperature, $1/2\pi\tau=21$ GHz, and $\omega_0/2\pi=34$ GHz, is the full line in Fig. 2. This description leads to a good fit to the experimental results, but we stress that in the low-frequency spectral range more detailed experiments are required to test the applicability of alternative descriptions of the frequency-dependent response. In the high-frequency limit measured here, however, Eq. (6) gives an excellent account of our experimental findings. The fit also indicates that $\omega_0\tau<1$, so that, in contrast to other materials, the ac response is only weakly damped. This could have important consequences for the various models of CDW transport where the inertial effects are completely neglected.

Similiar fits have been obtained at other temperatures, and the detailed temperature dependence will be reported later. It is, however, immediately clear from Fig. 1 that with decreasing temperatures only a slight shift of the ω-dependent response to higher frequencies is observed. Also, σ_b increases with decreasing temperature, until approximately 50 K, where we are no longer able to do an accurate fit, in terms of Eq. (6). Consequently, with n_{CDW} only weakly temperature dependent below about 200 K, this implies that τ/m^* increases with decreasing temperature. This is in accordance with recent calculations of the CDW damping, which takes the interaction of the condensed phasons with termally ambient phonons into account.[10] The carrier density n_{CDW} may be evaluated from known structural data, giving $n_{CDW}=1.7\times10^{21}$.[6] Then, with τ evaluated from the frequency-dependent response and $\sigma_{RT}=350$ $(\Omega\ \mathrm{cm})^{-1}$, Eq. (1) leads to an effective mass $m^*=10^4\pm10^3$, an enormous value compared with those obtained for other materials. This, we believe, is due to the large single-particle gap which opens up at the Fermi level in this material. The dc conductivity measurements[6] lead to $\Delta=1600$ K, in close agreement with the analysis of magnetic susceptibility,[11] which leads to a mean-field gap of 1300 K. For comparison to Eq. (3) we use the value of Δ derived from the conductivity measurements, and we use the expression $\Delta=1.76kT_p$ to evaluate Δ in the CDW states of $NbSe_3$ and TaS_3, where the transition is more closely mean field.[4] Equation (4) suggests that in all materials $\lambda\simeq0.4\pm0.2$. Consequently, if Eq. (3) for the effective mass is appropriate, the measured effective mass should be proportional to Δ^2. This relation is shown in Fig. 3, where masses obtained well below both CDW transitions in $NbSe_3$, in o-TaS_3, and in $(TaSe_4)_2I$ are displayed. Although we do not have experimental values for the band masses, they are expected to be close to the free-electron mass. The full line is $m^*/m_e=5.62\times10^{-3}\Delta^2$, and with Eq. (3) this leads to an evaluation of $\lambda\omega_{2k_F}^2$. If $\hbar\omega_{2k_F}/k_b=50$ K, then $\lambda=0.29$, both reasonable values. Although the above analysis, because of ambiguities in n_{CDW} and ω_{2k_F}, has only a semiquantitative significance, we believe that our findings lend strong support to the theory developed by Lee, Rice, and Anderson.

The measurements at 60 and 94 GHz also yielded the temperature dependence of the imaginary part of the conductivity, $\mathrm{Im}\sigma$. The results are relatively featureless and are not presented here. For the 60-GHz measurements $\mathrm{Im}\sigma$ is 0 ± 10 $(\Omega\ \mathrm{cm})^{-1}$ above the Peirls transition. Below T_P, $\mathrm{Im}\sigma$ becomes negative and decreases until $\simeq230$ K, where it saturates at -130 ± 20 $(\Omega\ \mathrm{cm})^{-1}$ and remains constant to very low temperatures. At 90 GHz $\mathrm{Im}\sigma$ was

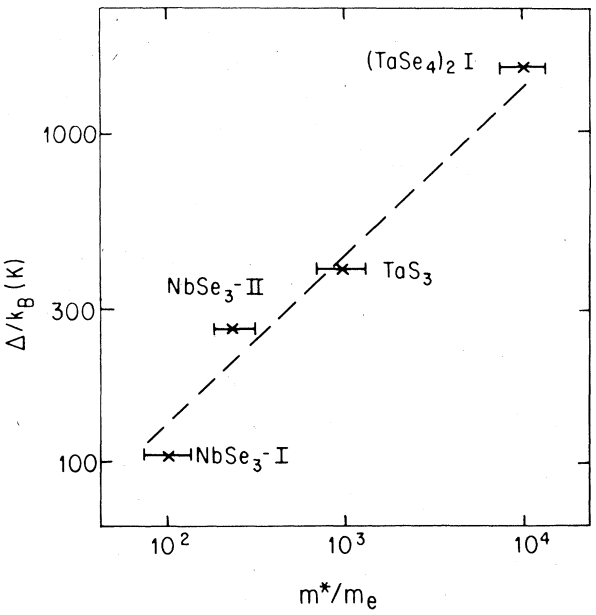

FIG. 3. The gap parameter Δ vs measured effective mass for various materials. The values for $NbSe_3$ and TaS_3 are from Ref. 4. Somewhat different effective-mass values have been obtained, using a different analysis, by Thorne *et al.* (Ref. 13). The error bars ($\pm 50\%$) result from the expected errors in the estimation of the carrier density and the measurement of the room-temperature dc conductivity.

also negative and weakly temperature dependent below the phase transition. The negative values of $\mathrm{Im}\sigma$ confirm the inertial response, and the relative variation indicates that the pinning-frequency and damping-temperature dependences are small, as suggested in the discussion of Fig. 1.

Finally, we comment on the pinning frequency ω_0 and the damping frequency $1/2\pi\tau$, which are larger and smaller, respectively, in this material than in other CDW compounds. The larger pinning frequency, we believe, is the consequence of a larger CDW amplitude ρ_1 which appears in the expression for the charge density:

$$\Delta\rho(x)=\rho_1\cos(2k_Fx+\phi)=\frac{\Delta}{\lambda^2\epsilon_F}\cos(2k_Fx+\phi)\ . \quad (7)$$

Because of the larger gap and roughly the same λ and ϵ_F in this material, ρ_1 is larger than in other compounds. The interaction of the CDW with impurity potentials, $V(x-x_i)=V_0\delta(x-x_i)$, is given by

$$H=V_0\rho_1\sum_i\cos[2k_Fx_i+\phi(x_i)] \quad (8)$$

and, consequently, for the same V_0 and impurity concentration c, a larger interaction energy and a larger pinning frequency result from a larger gap, as observed. The large ω_0 is consistent with the smaller low-frequency dielectric constant and larger threshold field[6,8] observed in this system.

The smaller damping in $(TaSe_4)_2I$ relative to that observed in other systems may also be understood in terms of a larger gap in this system. In the absence of normal electrons, the main source of damping comes from phason scattering,[10] and the inverse scattering time $1/2\pi\tau$ is given by

$$\frac{1}{2\pi\tau}=\frac{m_b}{m^*}\frac{8\lambda^2T^2}{2\Omega_t(\pi)^{3/2}}\ , \quad (9)$$

where Ω_t is the cutoff in the transverse phonon dispersion and T is the temperature. The scattering time, except for the factor of m_b/m^*, is of the same order as that found in the normal state, which for the same model is given by

$$\frac{1}{2\pi\tau_n}=2\lambda T\ . \quad (10)$$

An argument that $1/2\pi\tau$ should be smaller than $1/2\pi\tau_n$ by a factor of m_b/m^* has also been advanced by Bardeen.[12] The substantial difference between the CDW materials occurs in the effective mass, the other parameters having a weaker variation from material to material. We then expect that comparing o-TaS_3 to $(TaSe_4)_2I$ results in a reduction of $1/2\pi\tau$ by a factor of the ratio of the effective masses, approximately 0.1. From Ref. 4, at comparable temperatures, we have $1/2\pi\tau\simeq 130$ GHz for o-TaS_3, which yields a predicted damping for $(TaSe_4)_2I$ of $1/2\pi\tau\simeq 13$ GHz. The measured damping in $(TaSe_4)_2I$ is approximately 20 GHz, in order-of-magnitude agreement with the estimate from the ratio of the effective masses. The same comparison is not possible with $NbSe_3$, because the results in Ref. 10 neglect the effects of portions of the Fermi surface that remain attached below the phase transistion, which is the case with $NbSe_3$.

In conclusion, our frequency-dependent conductivity measurements on the inorganic linear chain comound $(TaSe_4)_2I$ suggest an underdamped collective CDW response. The effective mass is enormous, and reflects the strong electron-phonon coupling and consequently the large effective mass in this material. This also leads to a large pinning frequency ω_0 and a smaller damping, $1/\tau$. Our results strongly support the theory of Lee, Rice, and Anderson[5] concerning the effective mass of the CDW condensate. A detailed account of our experimental findings will be reported later.

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