Frequency-Dependent Response of Pinned Charge-Density-Wave Condensates: Classical versus Quantum Description

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Frequency-dependent conductivity measurements are reported in the charge-density-wave state of $Ta_{1-x}Nb_xS_3$ alloys at microwave and millimeter-wave frequencies. For increasing impurity concentration, the pinning frequency of the charge-density-wave collective response increases sharply while the damping of the response remains constant. Although both the classical and quantum tunneling models describe the small-amplitude ac response of the pure materials for $\omega < \omega_p$, our results clearly support a classical oscillator response for $\omega > \omega_p$ and for the alloys.

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The frequency- (ω) and electric-field- (E) dependent transport phenomena observed in many inorganic linear-chain compounds in their charge-density-wave (CDW) state give clear evidence for a novel type of collective transport.[1] This paper addresses the unresolved question of whether purely classical concepts are sufficient to describe the dynamics of the collective mode, or whether quantum effects play an important role.

One approach[2] treats the response of the pinned collective mode in terms of a classical harmonic oscillator with an effective mass m^*, pinning frequency ω_0, and damping constant $1/\tau$. A different description, referred to in the literature as the tunneling model,[3] suggests that the frequency-dependent conductivity, $\sigma_{\mathrm{CDW}}(\omega)$, is due to carrier excitations across a small pinning gap $\hbar\omega_0$ and that the field-dependent conductivity, $\sigma_{\mathrm{CDW}}(E)$, is due to macroscopic quantum tunneling across the gap. A set of experiments performed by Thorne *et al.*[4] in the radio-frequency spectral range in pure $NbSe_3$ and orthorhombic TaS_3 (O-TaS_3) have been successfully interpreted in terms of a revised version of the tunneling model.[5] The measurements and the comparison to the revised tunneling model, however, span a spectral range entirely below resonance, so that a comparison with the full frequency dependence is not possible.

We have performed frequency-dependent conductivity measurements on $Ta_{1-x}Nb_xS_3$ alloys in the microwave and millimeter-wave spectral range in an attempt to clarify the role of quantum phenomena in CDW dynamics. The alloys were chosen because certain parameters, such as the number of condensed electrons, n, and the effective mass, m^*, remain unchanged by alloying[6] and only the parameters which are most important in the analysis (see below) depend on the impurity concentration. These characteristics, together with the broad frequency range employed, allow a detailed comparison with the proposed models. We find that the damping is independent of the impurity concentration. In contrast, the pinning frequency is strongly concentration dependent. In the comparison with classical and quantum theories given below we conclude that the main adsorption observed in the alloys is due to the pinned CDW mode, the dynamics of which may be described in terms of classical concepts, with no tunneling processes involved.

Before we present the experimental results we will discuss the implications of the classical and quantum theories. In terms of a classical harmonic-oscillator approach,[2] the ω-dependent response of the CDW condensate is given by

$$\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega) = \frac{ne^2\tau}{m^*}\frac{\omega^2/\tau^2}{(\omega_0^2-\omega^2)^2+\omega^2/\tau^2}, \tag{1}$$

where ω_0 and τ are phenomenological constants representing the pinning and damping of the collective mode. The effective mass normalized to the band mass m_b is given in terms of the fundamental parameters single-particle bandwidth (D), phonon frequency ($\omega 2k_{\mathrm{F}}$), and electron-phonon coupling constant (λ) as[7]

$$\frac{m^*}{m_b} = 1 + \frac{4D^2\exp(-2/\lambda)}{\omega 2k_{\mathrm{F}}^2\lambda}. \tag{2}$$

None of the parameters on the right-hand side depends strongly on impurities, and consequently m^*/m_b is also expected to be independent of the impurity concentration.

The ω-dependent response, as given by Eq. (1), is characterized by three frequencies. In the high-frequency limit, the Drude-type rolloff is determined by $1/\tau$. The conductivity has a peak at $\omega=\omega_0$ with

$$\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega=\omega_0) = ne^2\tau/m^*. \tag{3}$$

At $\omega=0$, $\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega)=0$, and the behavior for $\omega<\omega_0$ may be characterized by the frequency $\omega_{1/2}$, where

$$\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega_{1/2}) = \tfrac{1}{2}\,\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega_0).$$

In terms of Eq. (1) this frequency corresponds to the so-called crossover frequency, $\omega_{1/2}=\omega_{c0}=\omega_0^2\tau$. We note that the description in terms of Eq. (1) is purely phenomenological and contains no predictions about the relation between ω_0 and $1/\tau$.

In its latest version,[5] the tunneling model specifically predicts the relation between ω_0 and $1/\tau$. The parameters which characterize the ω-dependent response are determined by an effective length scale, L_0, of order of the Lee-Rice coherence length. With $L_0=(m_b/m^*)^{1/2}v_F/\omega_0$ and $L_0=2v_F\tau$, where v_F is the Fermi velocity, we have

$$2\omega_0=(m_b/m^*)^{1/2}\tau^{-1}. \quad (4)$$

Thus, for constant m^*/m_b an increase of ω_0 upon alloying leads to a corresponding increase of $1/\tau$, and consequently, through Eq. (3), to a decrease of the maximum conductivity. The behavior for $\omega<\omega_0$ is described by the expression

$$\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)=(ne^2\tau/m^*)\exp(-\omega_s/\omega), \quad (5)$$

where the so-called scaling frequency (ω_s) is the frequency where $\sigma_{\mathrm{CDW}}(\omega)$ is equal to e^{-1} times its $\sigma_{\mathrm{CDW}}(\omega=\omega_0)$ value. With use of Eqs. (3) and (5), the revised quantum theory[5] predicts

$$\omega_{1/2}=1.4\omega_s=1.4(m/m^*)^{1/2}\omega_0 \quad (6)$$

and the ratio $\omega_{1/2}/\omega_0$ is independent of both frequency and impurity concentration.

Before discussing the experimental results for the alloys we will review the measurements performed on pure O-$\mathrm{TaS_3}$.[8] In Fig. 1 we show $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$ measured at $T=160$ K in detail. The three characteristic frequencies, $1/\tau$, ω_0, and $\omega_{1/2}$, are also shown in the figure. The full line is a fit by Eq. (1) with $\omega_0/2\pi=5.3$ GHz, $1/2\pi\tau=120$ GHz, $\sigma_{\max}=\sigma_{\mathrm{CDW}}(\omega=\omega_0)=2500$ $(\Omega\ \mathrm{cm})^{-1}$, and an effective mass $m^*/m_b=940$. The fit is appropriate at high frequencies, but for $\omega\leqslant\omega_0$ the observed frequency dependence is more gradual than that given by the harmonic-oscillator approach, Eq. (1). The behavior in this region may be modeled with a distribution of $\omega_0^2\tau$, or equivalently, with a distribution in ω_0 having a cutoff frequency near the frequency of the peak in $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$.[8] The tunneling model also gives a good fit in this frequency region, as shown by the dashed line in the figure, with $\omega_s=160$ MHz. From Eq. (4), the parameters $1/2\pi\tau=120$ GHz and $\omega_0/2\pi\sim3$ to 10 GHz lead to an effective mass $m^*/m=35$ to 400, in broad agreement with the prediction obtained from the classical description. Also, with $\omega_{1/2}=230$ MHz and $\omega_0/2\pi=5$ GHz, Eq. (6) leads to $m^*/m=930$, in agreement with the previous values and also in good agreement with the effective mass evaluated by Thorne *et al.*[4] Thus, the tunneling theory gives an appropriate description of $\sigma_{\mathrm{CDW}}(\omega)$ in the pure material. As will be discussed below, this is not the case for the alloys where the observed concentration dependences are in clear conflict with the predictions of the tunneling model.

The experiments were performed on $\mathrm{Ta_{1-x}Nb_xS_3}$ alloys with nominal Nb concentrations of $x=0.001$ and $x=0.002$. The samples were grown by standard gradient-furnace techniques and dc measurements have been reported.[9] A small depression of T_c and large increase of E_T are evidence for small increases in the impurity concentration, in agreement with direct irradiation studies. The nominal concentrations correspond to the concentration of Nb placed in the crystal-growth medium and may be different from the actual impurity content in the specimens; this, however, does not alter the arguments presented below. The conductivity measurements were performed by both cavity-perturbation and impedance-bridge techniques described earlier.[10,11]

In Fig. 2, $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$ measured on the pure materi-

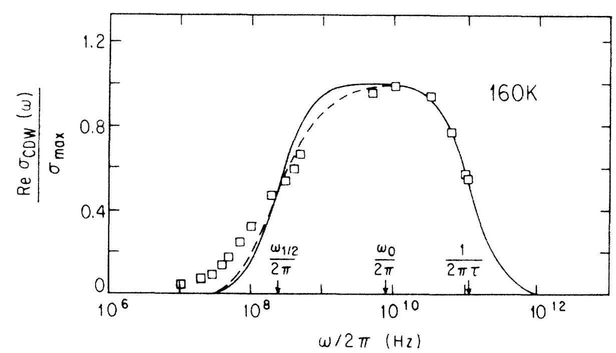

FIG. 1. Frequency-dependent conductivity of nominally pure O-$\mathrm{TaS_3}$. The characteristic frequencies are indicated on the figure and correspond to $1/2\pi\tau=120$ GHz, $\omega_0/2\pi=8$ GHz, and $\omega_{1/2}/2\pi=230$ MHz. The full line is a fit by Eq. (1) (classical harmonic-oscillator model) and the dashed line is a fit by Eq. (5) (tunneling model).

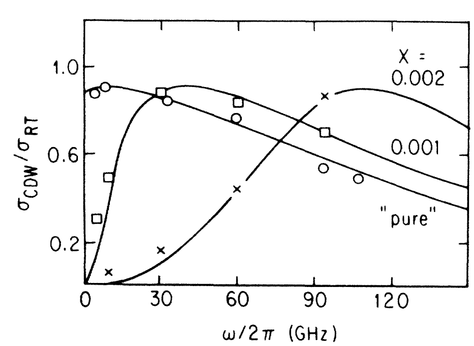

FIG. 2. Frequency-dependent conductivity of $\mathrm{Ta_{1-x}Nb_xS_3}$ alloys measured at $T=160$ K. The full lines are fits by Eq. (1).

al and on the alloys is displayed. We observe a dramatic shift of the frequency dependence to higher frequencies, suggesting a strong increase of ω_0 and $\omega_{1/2}$ with alloying, in agreement with the general concept of impurity pinning.[1] The maximum value of the conductivity, on the other hand, is hardly affected by the impurities, suggesting that pinning and damping are not intimately related and that $1/\tau$ is of intrinsic origin. $\mathrm{Im}\sigma_{\mathrm{CDW}}(\omega)$ was also measured and is in full agreement with the values deduced from the Kramers-Kronig relations and $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$. The results for $\mathrm{Im}\sigma_{\mathrm{CDW}}(\omega)$ will be presented in a later publication, along with the temperature dependence of the $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$.

The concentration dependence of the parameters $1/\tau$, ω_0, and $\omega_{1/2}$ have been evaluated with use of Fig. 2 as well as earlier measurements of the low-frequency dielectric constant. For the pure specimens and the $x=0.001$ specimens the pinning frequency ω_0 may be obtained directly from Figs. 1 and 2 by examining where $\mathrm{Re}\sigma_{\mathrm{CDW}}(\omega)$ has a maximum. For the alloy with $x=0.002$, the experimental results indicate that ω_0 is above our highest measurement frequency. However, we may use the low-frequency dielectric constant

$$\epsilon(\omega << \omega_0^2\tau) = 1 + C(4\pi ne^2/m^*\omega_0^2) \qquad (7)$$

to evaluate the concentration dependence of the pinning frequency. Equation (7) is a consequence of the oscillator sum rule, and is valid for both the classical model and the tunneling model with C close to 1 in both cases.[1] Using earlier results,[6] and $\omega_0 \simeq 35$ GHz for the alloy with $x=0.001$, we obtain $\omega_0 \simeq 120$ GHz for the alloy with the higher impurity concentration.

The concentration dependence of the pinning frequency is displayed in Fig. 2. The characteristic frequency $\omega_{1/2}$, also shown in the figure, is obtained directly from Figs. 1 and 2 by interpolating between the nearest data points (and consequently is independent of the fit with the classical oscillator response displayed in Fig. 2). The values obtained by this method are also displayed in Fig. 3. The error bars in the figure correspond to the most extreme values that could be chosen for the characteristic frequencies.

The full lines in Fig. 2 are fits by Eq. (1). They lead, for the pure specimens and for the $x=0.001$ alloy, to the $1/\tau$ values displayed in Fig. 3. An analysis with Eq. (3) and the maximum conductivity in Fig. 2 leads to $m^*/m=940$ and 960, respectively, in agreement with previous results. The quantity $1/\tau$ cannot be directly evaluated for the alloy $Ta_{0.998}Nb_{0.002}S_3$ because of the limited frequency range measured. The quantities n and m^*, however, depend only on the order parameter, which in turn varies by only a few percent for these impurity concentrations.[7] The maximum conductivity given in Eq. (3) varies inversely with $1/\tau$ with all other factors constant. $\mathrm{Re}\sigma_{\mathrm{CDW}}(94$ GHz), therefore, gives an upper limit for $1/\tau$ in the $x=0.002$ samples, which is also displayed in Fig. 3. Furthermore, the pinning frequency is approximately 120 GHz for the $x=0.002$ specimens, which implies that $\sigma_{\mathrm{CDW}}(94$ GHz) is within 10% of the maximum conductivity. The observation that the maximum conductivity for all the pure and doped samples is independent of the impurity concentration reinforces the observation that $1/\tau$ is independent of the impurity concentration.

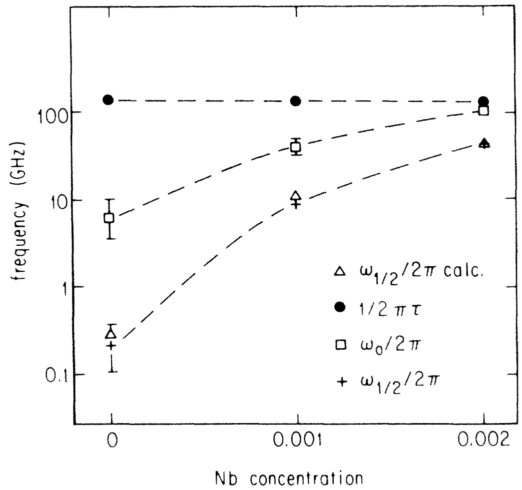

FIG. 3. Concentration dependence of the characteristic frequencies $1/\tau$, ω_0, and $\omega_{1/2}$. The error bars refer to the uncertainties in evaluating the parameters when the response is very broad (see text). The dashed lines are guides to the eye. "$\omega_{1/2}/2\pi$ calculated" refers to the crossover frequency calculated from Eq. (1) with use of the measured values of ω_0 and $1/\tau$.

Regarding the concentration dependence of the characteristic frequencies $1/\tau$, ω_0, and $\omega_{1/2}$, the following aspects of Fig. 3 should be noted.

(a) $1/\tau$ is independent (within an experimental error of $\pm 10\%$) of the impurity concentration, suggesting a damping of an intrinsic origin,[12] while ω_0 increases by approximately 1 order of magnitude. The increase of ω_0 is well understood as being a consequence of pinning by impurities. The fact that $1/\tau$ is concentration independent and ω_0 is not is in clear contrast with the prediction of the tunneling model, Eq. (4).

(b) The characteristic frequency, $\omega_{1/2}$, increases with increasing concentration approximately as the square of ω_0 for the pure and $x=0.001$ samples. This behavior is in clear agreement with a strongly damped classical response, where $\omega_{1/2}=\omega_0^2\tau$ and τ is independent of the impurity concentration. At larger impurity concentrations ($x=0.002$) the quality factor (Q) of the resonance approaches unity, and $\omega_{1/2}$ is approximately equal to $\omega_0 - 1/2\tau$, also in agreement with the classical model. $\omega_{1/2}$ calculated from the measured pinning frequency and damping is displayed in Fig. 3. The observed concentration dependence is, however, in conflict with the tunneling model, which predicts that $\omega_{1/2}$ and ω_0 are proportional to each other [see Eq. (5)].

We conclude, therefore, that the small-amplitude frequency-dependent response observed in O-TaS_3 alloys in the microwave and millimeter-wave spectral range is due to the pinned collective mode which oscillates around the pinning positions. The classical harmonic-oscillator response correctly describes the main features of $\sigma_{CDW}(\omega)$ in this frequency region, with the phenomenological parameters $1/\tau$ and ω_0 representing the damping and pinning of the collective mode. The effect of impurity pinning is clearly evident at low frequencies, where $\sigma(\omega)$ may be analyzed in terms of a distribution of relaxation times. This, we believe, may be related to the nonlinear response, where E_T is smaller than inferred from a classical particle description and the functional form of $\sigma(E)$ is different. Alternatively, tunneling events may be important in this parameter region. The observed behavior in the microwave and millimeter-wave regime, however, is in clear contrast to the predictions of the modified tunneling model, and we conclude that at millimeter-wave frequencies tunneling events do not contribute significantly to the measured frequency-dependent conductivity.

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