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Optical probing of thermal lattice fluctuations in charge-density-wave condensates

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Thermal lattice fluctuations in charge-density-wave (CDW) condensates have been studied by means of optical investigations on the prototype CDW compound $K_{0.3}MoO_3$ and its alloys. The temperature dependence of the CDW gap absorption in the mid-IR frequency range is strongly indicative of the important role played by the thermal lattice fluctuation effects. The latter remove the inverse-square-root singularity, expected for the case of the static distorted lattice. In fact, a considerable broadening (i.e., larger than k_BT) of the subgap tail absorption is found by increasing the temperature towards T_{CDW}. Moreover, we find that the phase phonon modes also give an important contribution to the disorder parameter, thus being an essential ingredient for the thermal fluctuation effects.

Many quasi-one-dimensional materials undergo a structural instability known as the Peierls or charge-density-wave (CDW) instability.[1] Among a large variety of one-dimensional systems the so-called blue-bronze compound $K_{0.3}MoO_3$ is the prototype CDW material. It undergoes a CDW transition at $T_{CDW} = 180$ K and on this system the most detailed analysis up to date has been performed.

A central aspect of the CDW phase transition is the appearance of the so-called fluctuation effects. Here, we want to address our attention to the thermal lattice fluctuations. In the great majority of one-dimensional compounds the zero-point lattice motion is of the same order of magnitude of the Peierls distortion and consequently one might expect possible huge effects on the electronic density of states. Recently, it has been suggested that thermal lattice fluctuations should clearly manifest in the absorption characteristic of the CDW gap (which is opened at the Fermi surface due to the periodic lattice distortion with twice Fermi wave vector $2k_F$).[2] Indeed, the appearance of substantial subgap-tail absorptions is predicted. These subgap-tail absorptions, which broaden by increasing the temperature, determine a remarkable deviation from the expected inverse-square-root singularity at 2Δ, suggested by the static mean-field approach.[3] However, the theory (Ref. 2) was contrasted until now with experiments on compounds that have a substantial intrinsic disorder (like, e.g., KCP). This intrinsic disorder leads to effects similar to the thermally induced disorder, complicating the analysis, in particular as far as the effect of the zero-point lattice fluctuations are concerned.

In this paper we report on our first attempt to study these features in more depth by probing the effects of the thermal lattice fluctuations with optical methods on the model compound $K_{0.3}MoO_3$ and its alloys, where, furthermore, the static disorder due to random positions of the counterions is *absent*. Moreover, from our obervations we find that the phase phonon modes (phasons)[4] also contribute considerably to the thermal fluctuations and play an important and decisive role in the temperature dependence of the disorder parameter. In this respect, our experimental data agree with a recent theoretical prediction.[2,5]

The $K_{0.3}MoO_3$ specimens used in this study have been grown by electrolytic reduction of the starting materials (i.e., K_2MoO_4 and MoO_3), as described in detail in Ref. 4. Reflectivity measurements as a function of temperature and with light polarized parallel to the chain direction were then performed in a broad photon energy range from 10^5 down to approximately 15 cm^{-1}, using several spectrometers with overlapping energy ranges.[4] The reflectivity measured over such a broad energy spectral range has been used for the Kramers-Kronig transformations, from which we obtain the optical functions [$\varepsilon(\omega)$ and $\sigma(\omega)$].

The complete excitation spectrum of $K_{0.3}MoO_3$ has

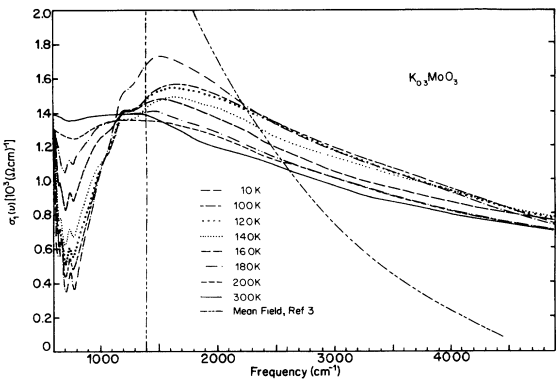

FIG. 1. Optical conductivity in the mid-IR for $K_{0.3}MoO_3$. The mean-field result of Ref. 3 for the static distorted lattice is also shown and displays the inverse-square-root singularity.

been presented and thoroughly discussed elsewhere.[4] For the present discussion, we will concentrate our attention on the mid-IR spectral frequency window. In this respect, Fig. 1 displays the optical conductivity in that range at several temperatures above and below $T_{\rm CDW}$. No remarkable difference has been obtained in the W-doped alloys. By lowering the temperature below $T_{\rm CDW}$ the optical conductivity drops dramatically and one observes the progressive formation of a broad excitation at ~ 0.2 eV.[4] The latter is ascribed to the CDW gap absorption 2Δ. In fact, the onset of that absorption coincides with the gap value evaluated from the activated behavior of dc transport properties.[4] We observe that this gap absorption seems to persist also above $T_{\rm CDW}$, at least up to 200 K.[4,6] Moreover, a recent scanning tunneling microscopy experiment is indicative of a gap of 140±20 meV in the electronic density of states.[7]

As clearly manifested in Fig. 1, the observed optical conductivity in the mid-IR frequency range is quite different from what is given by the mean-field theory, for which at all temperatures below $T_{\rm CDW}$ the absorption is predicted to be zero for $\omega < 2\Delta$ and has an inverse-square-root singularity at $\omega = 2\Delta$ (see Fig. 1).[3] Indeed, the singularity is absent, and there is a significant tail below the maximum. Furthermore, as the temperature increases, broadening of the spectrum occurs on an energy scale much larger than k_BT. The broadening is particularly remarkable for temperatures larger than approximately 50 K, and it is larger than what might be expected from anisotropy effects or interchain coupling.

We should also note that several other systems, e.g., KCP, $(CH)_x$, $(TaSe_4)_2I$, Pt-halogen chain,[8–12] show this particular behavior. However, while there is no accepted theory of the temperature dependence of the lattice distortion and the gap parameter, most of the previous experiments were compared to empirical formulas or the mean-field (BCS) form with a renormalized temperature. Attempts have been also made to explain some of these facts in terms of solitons, disorder, or imperfect nesting. Furthermore, some of those materials (like, e.g., KCP) are plagued by a quite important intrinsic static disorder.[8]

An interesting observation concerns the comparison of the lattice distortion u_0 and of the magnitude of the lattice zero-point motion $\delta u = (\hbar/2M\omega_A)^{1/2}$ (where M is the mass displaced and ω_A the amplitude mode frequency which determines the size of the actual zero-point motion), which are found to be comparable for most of the one-dimensional Peierls systems (e.g., for $K_{0.3}MoO_3$ $u_0 \approx \delta u \approx 0.05$ Å).[2] Given that the size of the electronic gap is proportional to u_0, lattice fluctuations should have an important effect on the electronic properties, and one might wonder why there should be a clearly developed gap excitation in the spectrum at all.

Recently, McKenzie and Wilkins showed that, starting from the Peierls-Fröhlich Hamiltonian with electron-phonon coupling as introduced by Brazovskii and Dzyaloshinskii,[13] the zero-point and the thermal lattice motions are a source of disorder.[2] There is a significant modification of the electronic density of states from the behavior predicted for a rigid distorted lattice. First, there is no large peak at the gap edges, in contrast to the inverse-square-root singularity which occurs in the absence of the zero-point motion.[3] Second, the density of states is nonzero for all energies and has a substantial subgap tail. Third, when temperature becomes of the order of the phonon frequency ω_A (for $K_{0.3}MoO_3$ $\omega_A \sim 80$ K), the disorder increases, and the smearing of the density of states increases considerably.[2] As pointed out above, there are signatures of such effects in the optical conductivity.

The strength of the disorder is proportional to $1/\tau$, the electron-phonon scattering rate for states well above the gap. The dimensionless disorder parameter,[2]

$$\eta = \frac{1}{\tau\Delta} = \lambda\frac{\pi\hbar\omega_A}{2\Delta}\coth\left(\frac{\hbar\omega_A}{2T}\right), \qquad (1)$$

determines the properties of the subgap states (where λ is the dimensionless electron-phonon coupling). At $T = 0$ it is also possible to write $\eta = (2\Delta/\tilde{W})(\delta u/u_0)^2$ (where $\tilde{W}$ is the bandwidth). Hence, when $\tilde{W}$ is larger than the gap, as it usually is, the effect of the lattice fluctuations is reduced. This explains why a reasonably well-defined gap is still possible (i.e., measurable) when $\delta u \sim u_0$.

The calculation of the optical conductivity reproduces the basic features found in the calculation of the density of states.[5] Even more interesting is the universal scaling form of the strong subgap conductivity. In fact, by scaling the calculated conductivity at different temperatures by the corresponding peak value ($\sigma_{\rm peak}$) and the frequency by the half width (Γ) for the low-frequency side of the σ_1 peak, the scaled curves for all η values have a universal form independent of η below the peak frequency ($\omega_{\rm peak}$).[5] Figure 2 shows the scaling of the experimental optical conductivity (Fig. 1) for the pure blue bronze at several temperatures. As suggested theoretically, we recover also experimentally the universal behavior. For comparison, Fig. 2 also presents the model calculation with $\eta = 0.66$ ($T = 0$ K) and $\eta = 1.0$ ($T = 140$ K). The deviations of the experimental optical conductivity from the theoretical calculation above the gap (Fig. 2) are due to the electronic interband transitions, which are not considered in the model of Ref. 5. In fact, band-structure calculations by Whangbo and Schneemeyer show that there are several bands within 0.1 eV of the conduction band.[14]

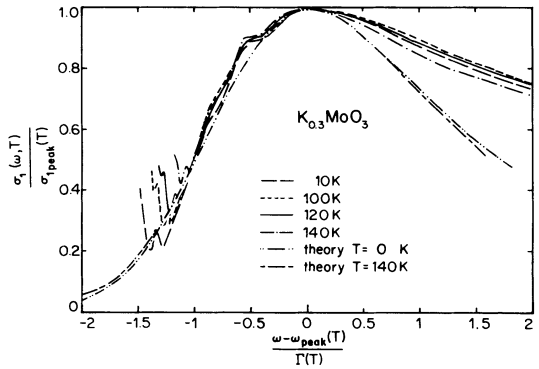

FIG. 2. Scaling plot of the experimental optical conductivity for $K_{0.3}MoO_3$ in the mid-IR. Note the universal form at several temperatures. A calculation with the model of Ref. 5 is also presented for the disorder parameter $\eta = 0.66$ ($T = 0$ K) and $\eta = 1.0$ ($T = 140$ K).

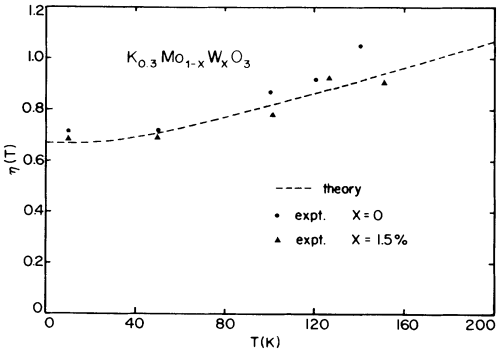

FIG. 3. Comparison between the experimental temperature dependence of the disorder parameter $\eta(T)$ and the corresponding theoretical curve [Eq. (2)]. The fit parameters are given in the text and in Table I. The full dots refer to the pure $K_{0.3}MoO_3$, while the triangles refer to $K_{0.3}Mo_{1-x}W_xO_3$ with $x = 1.5\%$.

Similar results can be found by rescaling the optical conductivity of other one-dimensional systems as well, like, e.g., KCP,[8] Pt-halogen chain,[12] $(CH)_x$.[9]

From the evaluation of the data leading to the universal scaling form discussed above, it is then possible to extract the temperature dependence of the disorder parameter. This is obtained by choosing η such that the computed $\Gamma(\eta)/\omega_{peak}(\eta)$ is equal to $\Gamma(T)/\omega_{peak}(T)$.[5,15] The experimental values of $\eta(T)$ (full dots refer to $K_{0.3}MoO_3$, and triangles to $K_{0.3}Mo_{1-x}W_xO_3$, with $x = 1.5\%$) are shown in Fig. 3. A comparison of the experimental values of $\eta(T)$ with the theoretical prediction of Eq. (1) using reasonable parameters would not be very satisfactory, unless one assumes an additional and very large extrinsic disorder (η_e), for which it would be difficult to find a plausible justification. However, it is possible to take into account the effect of the so-called phasons within the same theoretical framework leading to Eq. (1).[2,15,16] The result is that the disorder parameter is now given by

$$\eta(T) = \eta_e + \eta_i + \sum_n \frac{\lambda_n \omega_n \pi}{2\Delta} \coth\left(\frac{\hbar\omega_n}{2T}\right) , \quad \omega_n < 2\Delta , \tag{2}$$

where η_i is the contribution of Eq. (1) and λ_n and ω_n are the dimensionless electron-phonon coupling and frequency, respectively, of the phasons.[16] The theoretical fit to the experimental points (dashed line in Fig. 3) of the pure and doped blue bronze has been obtained with $\eta_e = 0.1$, $\lambda = 0.5$, $\hbar\omega_A = 7.05$ meV (i.e., 82 K), and $2\Delta = 0.174$ eV. As in our previous work,[4] λ_n and ω_n were obtained by a fit of the optical conductivity in the CDW ground state after the phason model of Rice,[17] and those parameters are summarized in Table I. A good fit to the experimental values of $\eta(T)$ is achieved and this set of parameters also satisfies several experimental constraints. In fact, 2Δ and $\hbar\omega_A$ correspond to the gap evaluated from the activated behavior of the dc resistivity and to the measured amplitude mode frequency,[4,18,19] respectively. Furthermore, from the expression $\omega_A = \sqrt{\lambda_{tot}}\omega_{2kF}$ (ω_{2kF} being the unrenormalized phonon frequency responsible for the Kohn anomaly,[18] and $\lambda_{tot} = \lambda + \sum_n \lambda_n = 1.16$) we obtain $\hbar\omega_{2kF} = 6.6$ meV, in fair accord with the value arrived at with neutron scattering investigation.[18]

TABLE I. The dimensionless electron-phonon coupling λ_n, the frequency ω_n, and the damping Γ_n of the phase phonon modes calculated after the model of Ref. 17. A plasma frequency of $\nu_p = 2.1 \times 10^4$ cm^{-1} and a static dielectric function $\varepsilon_0 = 7 \times 10^4$ have been used (Refs. 4 and 17).

ω_n (cm^{-1})	λ_n	Γ_n (cm^{-1})	ω_n (cm^{-1})	λ_n	Γ_n (cm^{-1})
30	0.06	0.8	300	0.01	20
50	0.06	5.0	350	0.01	20
80	0.04	9.0	400	0.02	60
100	0.04	3.0	450	0.02	40
150	0.09	15	500	0.08	60
200	0.04	10	550	0.08	60
250	0.01	20	800	0.10	95

In conclusion, there seems to be evidence for a unique mechanism, leading to the remarkable signatures characterizing the dynamical conductivity and more generally the electronic density of states of the CDW systems. As we have shown from the optical point of view, the thermal lattice fluctuations, together with the phase phonon mode contribution, influence the excitation spectrum in a very wide temperature range and play a remarkable role in the temperature dependence of the disorder parameter. The blue bronze has been chosen as a prototype system, free from static disorder, although other CDW compounds are expected to show the same behavior. Particularly good candidates are those systems with an enhanced low dimensionality, like, e.g., $(TaSe_4)_2I$. On this latter compound, extensive optical investigations are in progress.

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