Single Particle and Collective Excitations in the One-Dimensional Charge Density Wave Solid $K_{0.3}MoO_3$ Probed in Real Time by Femtosecond Spectroscopy

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Ultrafast transient reflectivity changes caused by collective and single particle excitations in the quasi-one-dimensional charge-density wave (CDW) semiconductor $K_{0.3}MoO_3$ are investigated with optical pump-probe spectroscopy. The temperature dependence of nonequilibrium single particle excitations across the CDW gap and their recombination dynamics are reported for the first time. In addition, amplitude mode reflectivity oscillations are observed in real time. A T-dependent overdamped response is also observed which is attributed to relaxation of the phason mode.

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Molybdenum oxides like $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$ are well known for their interesting electronic properties arising from their one-dimensional (1D) chain structure [1]. At room temperature they are highly anisotropic 1D metals. Upon cooling, they become susceptible to a Peierls instability on the 1D chains causing fluctuating local charge-density wave (CDW) ordering. Upon further cooling, as fluctuations are reduced, interchain interactions cause the CDWs on individual chains to become correlated, eventually undergoing a second-order phase transition to a three-dimensionally (3D) ordered state below $T_c = 183$ K. The formation of a 3D CDW ordered state is concurrent with the appearance of a gap Δ_{CDW} in the single particle (SP) excitation spectrum, while the collective excitations of the 3D CDW state are described by an amplitudon mode (AM) and a phase mode (phason).

In this Letter we report femtosecond time-domain transient reflectivity measurements on $K_{0.3}MoO_3$ enabling for the first time real-time observation of the reflectivity modulations caused by collective CDW excitations. We report the T dependence of the amplitude $A(T)$, frequency $\omega_A(T)$, and damping constant $\tau_A(T)$ of the AM and for the first time the T dependence of the phason damping constant $\tau_p(T)$. We also report the T dependence of electron-hole recombination lifetime τ_s across the CDW gap below, as well as *above* T_c. Up till now, enhanced coherent phonon oscillations associated with the formation of a CDW were observed below T_{c1} in Mo_4O_{11} [2], but to our knowledge real-time observation of collective and SP excitations in CDW systems have not yet been reported.

In these experiments, an ultrashort laser *pump* pulse first excites electron-hole pairs via an interband transition in the material [step 1 in inset of Fig. 1(a)]. In a process which is similar in most materials including metals, semiconductors, and superconductors [3,4], these hot carriers very rapidly release their energy via *e-e* and *e-ph* collisions reaching states near the Fermi energy within $\tau_i = 10-100$ fs [step 2 in inset of Fig. 1(a)] acting as an ultrashort SP injection pulse. If a CDW or superconducting gap is present in the SP excitation spectrum, it inhibits the final relaxation step resulting in a relaxation bottleneck and photoexcited carriers accumulate above the gap [5]. This causes a transient change in reflectivity $\Delta\mathcal{R}/\mathcal{R}$ due to change in dielectric constant arising from excited state absorption processes of the type shown in step 3 in inset of Fig. 1(a). The density of these accumulated photoinduced (PI) carriers, n^*_{sp} can thus be determined as a function of temperature and time after photoexcitation from the transient reflectivity change $\Delta\mathcal{R}_s/\mathcal{R} \propto S(T)e^{-t/\tau_s}$, where τ_s is the characteristic SP recombination time. The amplitude is given by $S(T) \propto n^*_{sp}\rho_2|M_{12}|^2$, where M_{12} is the matrix element for the $E_1 \rightarrow E_2$ optical transition [Fig. 1(a)] and ρ_2 is the density of states in level E_2. Whereas ρ_2 and M_{12} can be assumed to be T independent in first approximation, n^*_{sp} is strongly T dependent when $k_BT \sim \Delta_{\mathrm{CDW}}$. A T dependence of n^*_{sp} has recently been calculated for various gap situations [5], which we can now compare with experiments.

In addition to the transient change of reflectivity due to SP excitations discussed above, a transient reflectivity signal is expected also from collective modes. The AM is of A_1 symmetry and involves displacements of ions about their equilibrium positions Q_0, which depend on the instantaneous surrounding electronic density $n(t)$. Since $\tau_i < \hbar/\omega_A$, the SP injection pulse may be thought of as a δ-function-like perturbation of the charge density n_{sp} and the injection pulse acts as a time-dependent displacive excitation of the ionic equilibrium position $Q_0(t)$. The response of the AM to this perturbation is a modulation of the reflectivity $\Delta\mathcal{R}_A/\mathcal{R}$ of the form $A(T)e^{-t/\tau_A}\cos(\omega_A t + \phi_0)$ by the displacive excitation of coherent phonons mechanism, known from femtosecond experiments on semiconductors [6] and superconductors [7].

The δ-function-like SP injection pulse also gives rise to the displacement of charges with respect to the ions, directly exciting the CDW phason. Since this is infrared active, we expect the resulting change of the

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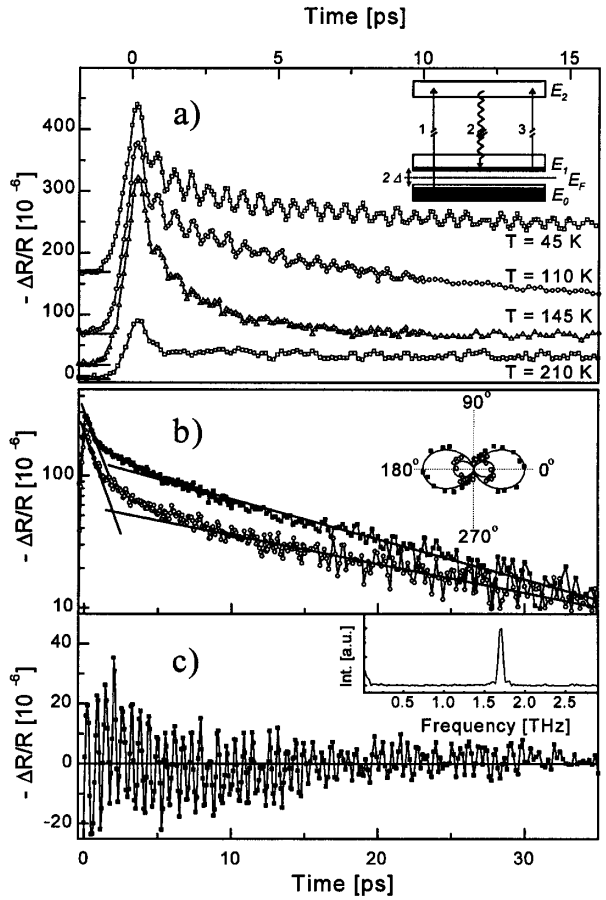

FIG. 1. (a) The transient reflection $\Delta R/R$ from $K_{0.3}MoO_3$ after photoexcitation by a 100 fs laser pulse at a number of temperatures above and below $T_c^{3D} = 183$ K. The constant background signal $B(T)$ was subtracted and offset for clarity. The inset shows the schematic of the photoexcitation and relaxation processes (see text). (b) The time evolution of transient signal with the oscillatory component subtracted shown at $T = 45$ and 110 K, displayed on a logarithmic scale to emphasize the difference in relaxation times τ_p and τ_s. The inset shows the amplitude $S(T)$ as a function of probe pulse polarization below (solid squares) and above T_c^{3D} (open circles) with respect to the crystal [102] direction. (c) The oscillatory transient signal $\Delta R_A/R$ after subtraction of the decay components B, S, and P. The fit is made using the first term in Eq. (1). The inset shows the FFT spectrum of the signal.

dielectric constant $\Delta\epsilon/\epsilon$ to lead to a directly observable reflectivity transient, which for small $\Delta\epsilon$ can be approximated as $\Delta\mathcal{R}_p/\mathcal{R} \simeq \Delta\epsilon/\epsilon$. In equilibrium, we expect the phason to be pinned and at a finite frequency, but in a nonequilibrium situation such as here, where the excess carrier kinetic energy may easily exceed the depinning energy, the mode may be depinned. In this case we may expect an *overdamped* reflectivity transient written as $P(T)e^{-t/\tau_p}\cos(\omega_p t + \phi)$, with $\omega_p \to 0$, but with a damping constant which is expected to be similar to that of the AM $\tau_p \simeq \tau_A$, i.e., $\sim$10 ps [8].

Summing all the contributions, in $K_{0.3}MoO_3$ the photoinduced transient reflectivity signal is of the form

$$\Delta\mathcal{R}(t,T)/\mathcal{R} = A(T)e^{-t/\tau_A}\cos(\omega_A t + \phi_0) + P(T)e^{-t/\tau_p} + S(T)e^{-t/\tau_s} + B(T). \quad (1)$$

For completeness we have included an additional term $B(T)$ due to a long-lived background signal, which is also observed experimentally, and whose lifetime is longer than the interpulse separation of 12 ns. The different contributions to $\Delta\mathcal{R}/\mathcal{R}$ can be effectively distinguished experimentally by their very different time dynamics and polarization and temperature dependences.

In the experiments reported here a mode-locked Ti:sapphire laser with pulse length $\tau_L \lesssim 100$ fs at 800 nm was used. The PI change in reflectivity $\Delta\mathcal{R}/\mathcal{R}$ was measured using a photodiode and lock-in detection. The pump laser power was kept below 5 mW, exciting approximately 10^{18}–10^{19} carriers per cm^3 [9], and the pump/probe intensity ratio was $\sim$100. The steady-state heating effect was accounted for as described in Ref. [10]. The experiments were performed on freshly cleaved $K_{0.3}MoO_3$ single crystals with the laser polarization in the a-b plane, a being the [102] direction and b the chain direction [11]. The orientation of the crystal was determined by using an atomic force microscope, by the direction of the Mo-O chains.

In Fig. 1(a) we show $\Delta\mathcal{R}/\mathcal{R}$ as a function of time at different temperatures. Below T_c, an oscillatory component is observed on top of a negative induced reflection, the latter exhibiting a fast initial decay followed by a slower decay. As T_c is approached from below, the oscillatory signal disappears, while the fast transient signal remains observed well above T_c, as shown by the trace at 210 K. For a quantitative analysis, we separate the different components of the signal according to their T dependence and probe polarization anisotropies. In Fig. 1(b) we show the signal at $T = 45$ and 110 K with the oscillatory component and background $B(T)$ subtracted. The logarithmic plot enables us to clearly identify two components with substantially different lifetimes, one with $\tau_s \simeq 0.5$ ps and the other with $\tau_p \gtrsim 10$ ps at low T. Their amplitudes and relaxation times are analyzed by fitting two exponentials [Eq. (1)]. For reasons which will become apparent, we attribute them to the SP relaxation $S(T)$ and phason relaxation $P(T)$, respectively. We note that $P(T)$ displays no sign of oscillatory response, in accordance with the expectation that the phason relaxation is overdamped in this type of experiment. The inset shows the dependence of the amplitude of the fast signal on the probe pulse polarization, showing maximum amplitude for $\vec{E} \parallel a$. In Fig. 1(c) we have plotted only the oscillatory component with its fast Fourier transform (FFT) spectrum, showing a peak at $\nu_A = 1.7$ THz. In contrast to the transient signal the amplitude of the oscillatory signal is independent of polarization [Fig. 2(a)].

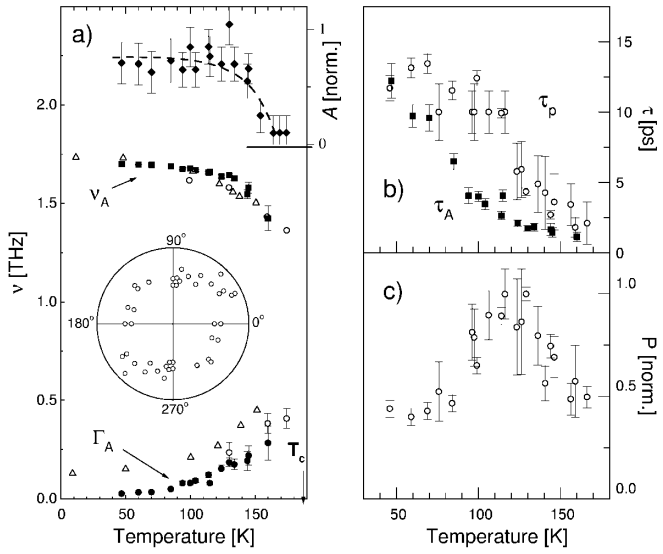

FIG. 2. (a) The amplitude $A(T)$ (diamonds), frequency ν_A (squares), and damping constant $\Gamma_A = 1/\pi\tau_A$ (full circles) as a function of T. Data from Refs. [12] (open circles) and [13] (open triangles) are also included. The inset shows the amplitude $A(T)$ as a function of probe polarization with respect to the crystal [102] direction. (b) τ_p as a function of T (circles). The amplitudon decay time τ_A is plotted for comparison (squares). (c) $P(T)$ as a function of T.

The T dependences of the single oscillatory component frequency ν_A and damping $\Gamma_A = 1/\pi\tau_A$ derived from fits to the real-time oscillations are shown in Fig. 2(a). Since the oscillation frequency ν_A shows clear softening as T_c is approached from below, the contribution from coherent phonons as observed in Ref. [2] can be excluded. The measured ν_A and Γ_A closely follow the expected behavior for the AM and are in good agreement with previous spectroscopic neutron [12] and Raman [13] data. The amplitude of the modulation $A(T)$ falls rather more rapidly with T than ν_A and is rather isotropic in the a-b plane [see inset of Fig. 2(a)].

In Figs. 2(b) and 2(c) we have plotted the T dependence of τ_p and $P(T)$. At $T = 50$ K, $\tau_p = 12 \pm 2$ ps, in agreement with the $\Gamma = 0.05$–0.1 THz linewidths of the pinned phason mode in microwave and IR experiments [1,12,14]. With increasing temperature τ_p is approximately constant up to 90 K and then falls rapidly as $T \rightarrow T_c$. The decrease of τ_p near T_c is consistent with increasing damping due to thermal phase fluctuations arising from coupling with the lattice and SP excitations. The amplitude $P(T)$ exhibits somewhat different behavior. It appears to first show an increase with increasing T, and then drops as $T \rightarrow T_c$. Such T-dependence behavior has been previously observed—but not yet satisfactorily explained—for the threshold field in some nonlinear conductivity experiments [15].

Let us now turn to the transient reflectivity signal due to photoexcited SP excitations. The T dependence of the PI signal amplitude below T_c for a T-dependent gap $\mathbf{\Delta}(T)$—for simplicity using a BCS-like T dependence—is given by [5]

$$S(T) \propto n_{sp}^{*} = \frac{\mathcal{E}_I/[\mathbf{\Delta}(T) + k_B T/2]}{1 + \gamma\sqrt{\frac{2k_B T}{\pi\mathbf{\Delta}(T)}}\,\exp[-\mathbf{\Delta}(T)/k_B T]}, \quad (2)$$

where $\mathcal{E}_I$ is the pump laser intensity per unit cell and γ is a constant, depending on the materials' parameters [5]. Plotting Eq. (2) as a function of temperature in Fig. 3(a), we find that the amplitude $S(T)$ obtained from the fits to the data agrees remarkably well with the theory for $T < T_c$: $S(T)$ is nearly constant up to nearly 100 K, then increases slightly and then drops very rapidly near T_c. The value of the gap $\Delta(0) = 850 \pm 100$ K obtained from the fit of Eq. (2) with $\gamma = 10$ is in good agreement with other measurements [1]. In contrast to the response of the collective modes $A(T)$ and $P(T)$, both of which disappear within 10–20 K below T_c, $S(T)$ remains observable up to nearly 240 K, i.e., appears to show a pseudogap up to 50 K above T_c. This is—in contrast to the behavior below T_c—clearly incompatible with a BCS-like description of the gap and suggests the fluctuating presence of the gap well above T_c. The polarization anisotropy of the signal $S(T)$ for $T > T_c$ is the same as for $T < T_c$ [Fig. 1(b)], strongly suggesting that the origin of the signal $S(T)$ above T_c is the same as below T_c, i.e., SP gap excitations.

The T dependence of the relaxation time τ_s [Fig. 3(b)] is qualitatively different to τ_p and τ_A. As $T \rightarrow T_c$, τ_s appears to *diverge* and then drops to $\tau_s \sim 0.25$ ps above T_c. Such behavior is in agreement with expected T dependence of SP relaxation across the gap. The dominant recombination mechanism across the gap is phonon emission via phonons whose energy $\hbar\omega_p > 2\Delta$ [5]. As the gap closes near T_c, more low-energy phonons become available for reabsorption and the recombination mechanism becomes less and less efficient. The recombination

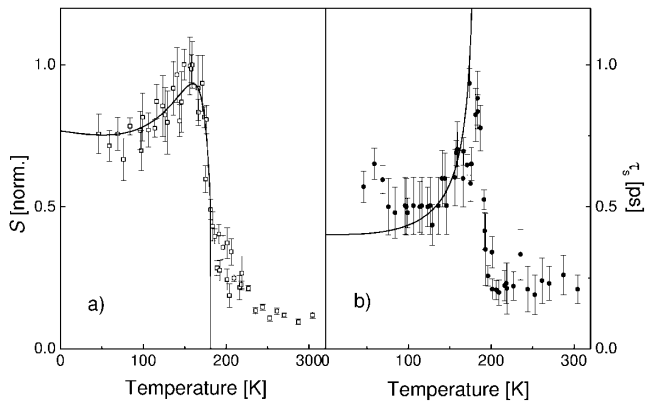

FIG. 3. (a) The T dependence of $S(T)$. The fit to the data for $S(T)$ is shown using Eq. (2) with a BCS-like gap $\Delta_{\mathrm{BCS}}(T)$ opening at $T_c^{3\mathrm{D}} = 183$ K. (b) The SP relaxation time τ_s as a function of T and a fit using Eq. (25) of Ref. [5].

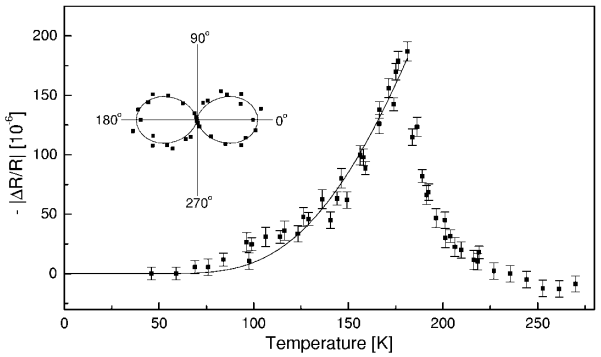

FIG. 4. The T dependence of the long-lived signal $B(T)$. The line is an Arrhenius fit of the signal amplitude below T_c with $E_a = 60$ meV. The inset shows the amplitude $B(T)$ as a function of probe pulse polarization with respect to the crystal [102] direction.

lifetime near T_c can be shown to be inversely proportional to the gap as $\tau_s \propto 1/\Delta(T)$ [5]. The solid line in Fig. 3(b) shows a fit to the data using a BCS-like T-dependent gap $\Delta_{\mathrm{BCS}}(T)$ with $T_c^{3\mathrm{D}} = 183$ K.

To complete the data analysis, we show in Fig. 4 the amplitude of the slowly decaying background signal $B(T)$ as a function of T. Its anomalous T dependence clearly rules out a thermal origin. The lifetime $\tau > 10^{-8}$ s deduced from the amplitude of $B(T)$ at "negative times," i.e., from the preceding pulse, strongly suggests excitations involving localized states. From a fit to an Arrhenius law $B(T) = B_0 \exp(-E_a/k_B T)$, we obtain an activation energy $E_a/\Delta(0) \sim 0.6 \pm 0.2$, suggesting that the process involves the excitation of carriers from intragap states into the SP continuum E_1. As the gap closes, excitations from intragap states to the SP states are no longer possible, explaining the T dependence of the signal above T_c. The microscopic origin of these states is most likely trapped defects, but the possibility of a collective excitation cannot be excluded at this stage. We note that a long-lived signal with a similar T dependence was recently observed in time-resolved experiments on the cuprate superconductor $YBa_2Cu_3O_{7-\delta}$ [16] and attributed to localized intragap states [17].

The real-time optical data present some qualitatively new information on the SP and collective excitations in quasi-1D materials. We have found that because of the qualitatively different time, polarization, and T characteristics, the responses of the different components can be effectively separated. Apart from directly extracting the T dependences of $A(T)$, $\nu_A(T)$, and $\tau_A(T)$, we also observe an overdamped mode, which we have assigned to relaxation of the phason mode. In addition to the observation of the T dependence of photoinduced SP population as predicted by theory [5], we find—also in agreement with calculations [5]—that the SP recombination time across the gap diverges as $\tau_s \propto 1/\Delta$ as $T \to T_c$. From the fact that the SP population appears to persist above T_c, the data show clear evidence for the existence of a pseudogap for SP excitations above T_c and suggest the fluctuating presence of a SP gap [18], rather than fluctuations of the order parameter, which would appear as a tail also in the SP relaxation time τ_s above T_c—but does not. Finally, we should mention that many of the features, particularly the T dependence of the SP excitation amplitude and the SP recombination lifetime is very similar to the behavior recently reported in cuprates [5,19]. We note that although coherent oscillations were reported in $YBa_2Cu_3O_{7-\delta}$, no T dependence of the oscillation frequency was reported, and they were attributed not to any collective electronic mode, but to c-axis phonons [7].

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