In superconductors (SC), it has been known for decades that an intense laser pulse can non-thermally destroy the superconducting ground state [1]. The energy required to destroy superconductivity should, in case all the absorbed optical energy is kept in the electronic subsystem during the process of superconductivity suppression, be equal to the condensation energy (energy difference between the free energy of the SC and normal states at $T = 0$ K). In recent experiments on MgB$_2$ [2] and the high temperature superconductor La$_{2−x}$Sr$_x$CuO$_4$ [3] it has been shown, however, that the absorbed optical energy required to suppress superconductivity is substantially higher than the thermodynamically measured condensation energy [3]. This discrepancy was accounted for by considering in detail all energy relaxation pathways on the timescale when superconductivity suppression is achieved. From this analysis it follows that on this timescale a quasi-equilibrium between the density of quasiparticles and high frequency phonons is achieved with most of the absorbed energy density being stored in the phonon subsystem [2, 3].

Charge density wave systems present another broken symmetry ground state. Here upon cooling through the CDW transition temperature the translational symmetry is broken [4]. The appearance of the long-range charge density modulation is accompanied by the appearance of the gap in the single particle excitation spectrum at the Fermi level, while the collective excitations of the CDW state are the so-called amplitude and phase mode [4]. While real-time studies of photoexcited quasiparticle and collective mode dynamics in CDW compounds have been quite extensive in the weak and moderate perturbation regime [5, 6, 7, 8, 9], a reasonable understanding of the underlying relaxation processes has been obtained, systematic studies in the high perturbation regime, where the energy of the optical excitation pulse is enough to drive the phase transition from the CDW ground state to the normal metallic state [10, 11] are still lacking.

In this Letter we report on the first systematic study of carrier and collective mode dynamics in a prototype quasi-1 dimensional CDW K$_{0.3}$MoO$_3$. Systematic temperature and excitation density dependent measurements of the photoinduced reflectivity changes reveal that the phase transition from the ground CDW state to the normal metallic state can be achieved on the femtosecond timescale. From the energy conservation law it follows that the phase transition is non-thermal in origin; i.e. the phase transition is not a result of a simple heating of the sample to above the critical temperature. The absorbed energy density required to optically induce the phase transition is found to be comparable to the electronic energy difference upon CDW condensation. These results give new insight in the ultrafast processes governing the relaxation dynamics in low dimensional CDW systems. In particular, the results suggest that on the timescale shorter than the period of the characteristic lattice vibrations ($\approx 0.6$ ps in K$_{0.3}$MoO$_3$, which is the inverse frequency of the amplitude mode [5, 12]) the charge density modulation is suppressed while the lattice remains unperturbed keeping the 2 $k_F$ modulation.

In the experiments described here, we utilized a degenerate optical pump-probe technique to study the excitation intensity and temperature dependence of the photoinduced reflectivity dynamics in single crystals of blue bronze K$_{0.3}$MoO$_3$. We used a commercial Ti:Sapphire amplifier producing 6 $\mu$J, 50 fs laser pulses at $\lambda = 800$ nm (photon energy of 1.55 eV) at a variable repetition rate between 9 and 250 kHz. The laser was used as a source of both excitation and probe pulses. Samples were mounted in an optical helium flow cryostat, with both excitation and probe beam entering the sample at near normal incidence. Due to the strong anisotropy of the induced changes in reflectivity with respect to light polarization [5], the probe laser beam was polarized along the chain [010] direction, while the excitation beam was polarized along the perpendicular [102] direction [13]. To ensure a homogeneous excitation profile, the diameter of the pump beam at the sample position was twice the diameter of the probe beam. To determine the photoexcitation density at the position of the sample with high precision we used a beam profiler. We fitted the beam profile with a Gaussian, and the excitation fluences, $F$, used throughout the paper correspond to the maximum fluence at the center of the beam. Low thermal con-
ductivity in $K_0.3\text{MoO}_3$ can lead to a pronounced increase of the equilibrium temperature in the probed volume, proportional to the average laser power. Therefore, the high excitation experiments were performed at a low repetition rate ($10\text{-}30$ kHz), where at $F = 1 \text{ mJ/cm}^2$ the temperature increase is $\lesssim 10$ K.

Figure 1 presents the induced reflectivity transients taken at 4 K at several excitation densities. At low excitation densities the data show the same behavior as previously reported [10]. The decay dynamics of the (incoherent) electronic response show a bi-exponential decay with timescales $\tau_1 \approx 0.3$ ps and $\tau_2 \approx 7$ ps. The former one, showing critical slowing down upon approaching $T_c$, was attributed to the recovery of the CDW gap, while the second one was initially tentatively attributed to an overdamped phase mode [3]. Recent detailed studies of the dynamics as a function of $F$ and applied external electric field however suggest that this longer timescale more likely presents the second stage of the CDW recovery [10]. On top of the incoherent transient an oscillatory (coherent) signal is observed whose Fourier transform, obtained by Fast Fourier Transform (FFT) analysis, shows several frequency components which can be attributed to the coherently excited amplitude mode (the strongest mode at 1.68 THz) and several other phonon modes [2, 10, 14].

While the photoinduced transient is linear in $F$ over several orders of magnitude [10], we observe pronounced changes upon increasing the excitation intensity into the 100 $\mu$J/cm$^2$ range. The electronic component shows clear saturation at $F \gtrsim 200 \mu$J/cm$^2$ with a maximum induced change in reflectivity approaching 18 % [17]. One is tempted to ascribe this saturation behavior in reflectivity change to the photoinduced suppression of the CDW order, where this difference in reflectivity corresponds to the change in reflectivity between the normal metallic and the CDW state. Since no measurement of the temperature dependence of reflectivity at optical frequencies is reported to date, we have performed thermomodulation measurements to determine the magnitude and sign of change in equilibrium reflectivity upon increasing the temperature to above $T_3^{3D}$. We measured the reflectivity difference between CDW and metallic state at 1.55 eV (800 nm) by heating the sample to above the phase transition using a CW laser. The data show that the reflectivity at 800 nm indeed decreases upon increasing the temperature. The change in reflectivity of $\sim 10$ % was observed upon heating from 160 K to just above $T_c$. At temperatures above $T_3^{3D}$ the corresponding change in equilibrium reflectivity was less than 1 %. Therefore the observed reflectivity change and its saturation behavior upon increasing the excitation fluence are consistent with the photoinduced CDW-M phase transition.

From the rise-time of the reflectivity transient it also follows that this transition happens on the 100 fs timescale after photoexcitation (rise-time is becoming shorter upon increasing $F$). The initial decay time, $\tau_1$, shows a pronounced increase near the threshold fluence, followed by a rapid drop as shown in inset to Fig. 1 (the secondary decay time $\tau_2$ shows only a slight decrease upon increasing $F$). This critical slowing down of relax-
FIG. 3: The time evolution of the FFT spectrum at 4K recorded at $F = 12 \, \mu J/cm^2$, $130 \, \mu J/cm^2$, $0.38 \, mJ/cm^2$, and $2.5 \, mJ/cm^2$ (panels a-d). The plots are obtained by time-windowed FFT analysis with a 5 ps time window. The AM is strongly suppressed at $F \geq 200 \, \mu J/cm^2$, while the high frequency modes are present up to $F \approx 3 \, mJ/cm^2$.

More information about the nature of the photoinduced CDW-M phase transition can be gained by looking at the evolution of the FFT spectrum with time at different $F$, which is presented in Fig. 3 for four different fluences. Here one clearly sees that the AM vanishes at $F \gtrsim 300 \, \mu J/cm^2$ while the two zone-folding modes persist up to $F \gtrsim 2.5 \, mJ/cm^2$ finally disappearing above $F \gtrsim 3 \, mJ/cm^2$. The fact that high frequency modes survive above the threshold fluence for the photoinduced CDW-M phase transition suggests that on a short timescale time following the photoinduced CDW-M transition and subsequent recovery on the sub-ps timescale (inset to Fig. 1) the lattice remains largely unperturbed. In other words, photoexcitation with a 50 fs optical pulse of $F > F_{sat}$ induces melting of the electronic density modulation, which partially recovers on the sub-ps timescale, while the lattice is - on this timescale - uncoupled from the electron subsystem and retains its $2k_F$ modulation. Only in the second step of relaxation, which proceeds on the 10 ps timescale, the CDW can be described with a single order parameter where electrons adiabatically follow the lattice.

Additional support to the assignment of the saturation behavior to the photoinduced CDW-M transition comes from the study of the oscillatory response, shown in Fig. 2. Here clear suppression of the amplitude mode, which presents a fingerprint of the CDW state, is observed at comparable fluences. Figure 2 shows the 2 dimensional surface plot of the FFT spectrum of the oscillatory signal as a function of excitation intensity over several orders of magnitude. Several sharp lines are observed, the strongest being that of the amplitude mode (AM) at about 1.68 THz (56 cm$^{-1}$). The two second strongest modes at 2.25 THz (74 cm$^{-1}$) and 2.55 THz (85 cm$^{-1}$) correspond to zone-folding modes [18, 19]. In addition, some weaker modes in the range between 3.5-4.5 THz are also observed as in Raman [18]. We should also mention the weak side modes observed in the vicinity of the AM as well as the two zone-folding modes. These are not artefacts due to FFT. From the ratio of their amplitudes with respect to the main peaks, and from the considerably weaker damping constants compared to the main modes we ascribe these to their corresponding surface modes.

While Fig. 2 clearly shows strong suppression and increased damping of the AM above $F \approx 200 \, \mu J/cm^2$, suppression of other phonons follow at the excitation densities that are about one order of magnitude higher in $F$.
responds to $E_{sat}$, using $E_{sat} = \int_{T_0}^{T_0 + \Delta T} c_p(T) dT$. Here $c_p$ is the total specific heat \cite{14}. At $T_0 = 4$ K and $E_{sat} \approx 60$ meV/u.c.v. we obtain $\Delta T \lesssim 40$ K, while at higher $T_0$ this value is considerably smaller ($\Delta T \lesssim 3$ K at 172 K and $E_{sat} \approx 20$ meV/u.c.v.). In fact, the absorbed energy density required to heat $K_{0.3}MoO_3$ from 4K to its phase transition $T_0^{3D} = 183K$ is about 600 meV/u.c.v., an order of magnitude higher than $E_{sat}$. It follows that the photoinduced CDW-M phase transition is non-thermally driven.

From the observation of coherently excited zone-folded modes at fluences up to one order of magnitude higher than $E_{sat}$ it follows, that on the sub-ps timescale after photoexcitation, the electrons are nearly uncoupled from the lattice. In this case $E_{sat}$ should be compared to the energy gain of the electronic subsystem upon CDW condensation, $E_{el}$. To estimate $E_{el}$ we used the mean-field expression in the weak coupling limit, given by Eq. 3.40 in Ref. \cite{4}:

$$E_{el} = -n(\epsilon_F)\Delta^2 \left(\frac{1}{2} + \log\frac{2\epsilon_F}{\Delta}\right).$$  

(1)

Here $n(\epsilon_F)$ is the normal state density of states at the Fermi energy, $\epsilon_F$, and $\Delta$ is the value of the CDW gap. Using $\Delta = 60$ meV, $\epsilon_F = 0.24 - 0.39$ eV and $n(\epsilon_F) = 4 - 6$ eV$^{-1}$/u.c.v., we obtain $E_{el}(4K) = 37 - 66$ meV/u.c.v.. This value is in excellent agreement with $E_{sat}(4K) \approx 60$ meV/u.c.v., giving further support to the argument that during photoinduced CDW melting the electronic order parameter is decoupled from the lattice on the sub-ps timescale. At $F \gtrsim 3$ mJ/cm$^2$, which corresponds to the absorbed energy density of 1 eV/u.c.v., other modes are also completely suppressed. This energy density is in good agreement with the calculated energy density required to heat up the excited volume to above $T_0^{3D}$. In this regime, recovery proceeds on a much longer timescale which is determined by heat diffusion out of the excited volume. The temperature dependence of $E_{sat}$, shown in Fig. 4b, shows good agreement with the expected T-dependence of $E_{el}$. The dashed line in Fig. 4b shows $E_{el}(T)$ calculated from Eq.(1), where the BCS T-dependence of $\Delta$ was used \cite{4}.

We have shown that in $K_{0.3}MoO_3$ the photoinduced CDW-M phase transition is non-thermally and takes place on the 100 fs timescale. The good agreement between measured $E_{sat}$ and calculated $E_{el}$, the observation of the order parameter recovery on the sub-ps timescale, and the observation of zone-folded phonons high above $E_{sat}$ suggest that during the process of melting and sub-ps recovery of the electronic modulation the lattice remains nearly frozen. This has an important implication for understanding the ultrafast relaxation processes in systems with reduced dimensionality, in particular for the systems with strong electron-phonon interactions that lead to phenomena like charge density modulation. The initial reconstruction of the CDW state is found in all systems studied thus far to proceed on the sub-ps timescale \cite{2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15}. Importantly, this timescale is one to two orders of magnitude faster than in the high-$T_c$ superconductors \cite{2}, and is indeed close to the typical timescale for electron-phonon thermalization. The formation of the CDW requires freezing of a phonon and our results do imply that the lattice remains frozen in its modulated state on the sub-ps timescale after perturbation. Therefore, the extremely fast order parameter recovery in this entire class of low-dimensional materials \cite{2, 3, 5, 6, 7, 8, 9, 10, 11} could be a consequence of the fact that on the short timescale after photoexcitation the lattice remains in its unperturbed state. Thereby, the retaining $2k_F$ modulation presents a strong potential well driving ultrafast reformation of the charge density modulation. Clearly, further theoretical studies as well as studies of the ultrafast structural dynamics are required to shed additional light on these fascinating phenomena.

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