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Michel van Veenendaal

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Photoinduced ultrafast charge-order melting: Charge-order inversion and non-thermal effects

Michel van Veenendaal^{1,2}

¹*Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, USA*

²*Advanced Photon Source, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439, USA*

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The effect of photoexcitation is studied for a system with checker board charge order induced by displacements of ligands around a metal site. The motion of the ligands is treated classically and the electronic charges are simplified to two-level molecular bond charges. The calculations are done for a checker-board charge-ordered system with about 100,000 ligand oscillators coupled to a fixed temperature bath. The initial photoexcitation is followed by a rapid decrease in the charge order parameter within 50–100 femtoseconds while leaving the correlation length almost unchanged. Depending on the fluence, a complete melting of the charge order occurs in less than a picosecond. While for low fluences, the system returns to its original state, for full melting, it recovers to its broken-symmetry state leading to an inversion of the charge order. For small long-range interactions, recovery can be slow due to domain formation.

I. INTRODUCTION

The phenomenon of ultrafast photoinduced charge-order melting is an intriguing example of nonequilibrium dynamics. The disappearance of long-range order has been observed in different classes of materials such as Peierls systems, where the material is unstable towards dimerization leading to an opening of a gap in the density of states, and systems where the charge order is a result of local displacements of the ligands around the metal sites. Despite the significant experimental progress in ultrafast pump-probe type experiments^{1–22}, our understanding of the phenomena following the excitation is still lacking. Treating the electronic and charge degrees of freedom at a quantum level is only feasible for system sizes of only several tens of atoms^{23,24} or under the assumption of a homogeneous system^{25,26}. Additionally, inclusion of relaxation is difficult for quantum systems. Another approach is to assume that the system can be described by an effective order parameter. Although such a phenomenological approach has been quite successful in describing the long-range order in pump-probe experiments^{10,15,22}, the assumption of a macroscopic order parameter obscures what is happening at a microscopic level. In this Report, we study a system combining molecular bond charges between neighboring metal sites with classical damped oscillators allowing system sizes sufficiently large from a thermodynamic stand point while providing insight in the charge-order melting at an atomic level. It was shown^{27,28} that Ising-like models can describe photoinduced nucleation. Here, the focus is on the thermodynamic aspects of photoinduced charge-order melting.

The outline of the paper is as follows. In the next Section, the model Hamiltonian is introduced. Since the focus is on thermodynamic effects and requires large systems, the typical model with electron-phonon interactions needs is simplified into a system with classical lig-

and oscillators and molecular bond charges. Section III describes how charge-order melting occurs in this system and focuses on the different types of recovery from the photoinduced state. The changes in correlation lengths are also discussed. The difference between charge-order melting from photoexcitation and heating is also discussed.

II. MODEL

The model under consideration forms a typical checker-board charge order below the critical temperature, the insets in Fig. 1. The metal sites form a square lattice where the position vectors are $\mathbf{R} = n_x \mathbf{e}_x + n_y \mathbf{e}_y$ where $\mathbf{e}_i$ ($i = x, y$) are the unit vectors in the x and y direction. The lattice constant is taking as unity. Without distortion, the ligands are located between the metal sites at $\pm \frac{1}{2} \mathbf{e}_x, \pm \frac{1}{2} \mathbf{e}_y$ around each metal site. The charge order is a result of the interaction between the electronic degrees of freedom and the lattice, where excess charge density on a metal site leads to a local distortion around the metal site, indicated by the arrows in the insets in Fig. 1. A simple Hamiltonian for a system with interacting electron and lattice degrees of freedom is

$$H = H_{\text{el}} + H_{\text{ph}} + H_{\text{el-ph}}. \quad (1)$$

The electronic part is given by the quantum-mechanical hopping between neighboring site

$$H_{\text{el}} = - \sum_{\mathbf{R}} \sum_{\delta=\pm\mathbf{e}_x, \pm\mathbf{e}_y} t c_{\mathbf{R}+\delta}^\dagger c_{\mathbf{R}}. \quad (2)$$

The phonon contribution is that of a classical oscillator

$$H_{\text{ph}} = \sum_{\mathbf{R}} \sum_{\delta=\mathbf{e}_x, \mathbf{e}_y} \left(\frac{1}{2m} d_{\mathbf{R}+\frac{1}{2}\delta}^2 + \frac{1}{2} m \omega^2 d_{\mathbf{R}+\frac{1}{2}\delta}^2 \right), \quad (3)$$

where $d_{\mathbf{R}+\frac{1}{2}\delta}$ is the displacement of the ligand and $\dot{d}_{\mathbf{R}+\frac{1}{2}\delta}$ is the velocity. Note that $d_{\mathbf{R}+\frac{1}{2}\mathbf{e}_i}$ is in the x and y direction for $i = x, y$, respectively. The electron-phonon term is given by

$$H_{\text{el-ph}} = -\lambda \sum_{\mathbf{R}} \sum_{\delta=\pm\mathbf{e}_x, \pm\mathbf{e}_y} s_{\delta} n_{\mathbf{R}} d_{\mathbf{R}+\frac{1}{2}\delta}. \quad (4)$$

The first term describes the electronic system in terms of a nearest-neighbor hopping integral $-t$ with $t > 0$. The operator $c_{\mathbf{R}}^{\dagger}$ creates an electron on site $\mathbf{R}$. The second term is the interaction between $n_{\mathbf{R}}$, the electron density at site $\mathbf{R}$, and the displacement $d_{\mathbf{R}+\frac{1}{2}\delta}$ of the classical oscillators. The factor $s_{\pm\mathbf{e}_i} = \pm 1$ with $i = x, y$ ensures that the energy is lowered when the ligands move away from the charge on the metal sites.

In the remainder, the oscillators are treated classically, but simplifications will be made to the electronic system. This will be done in two steps. First, instead of describing the charge fluctuations in terms of excitations of electron-hole pairs with respect to Fermi sea, they will be described in terms of molecular bond charges that describe the changes in electron density at the two metal ions neighboring a ligand oscillator. The following paragraphs justify this approach in the narrow-band limit where the changes in charge density are localized close to the ligands. The second part involves the dynamics. It is assumed that the motion of the ligand oscillators are well described in the classical limit. For the electron dynamics, the focus is on the processes that describe the thermalization: the photoexcitations and the thermal scattering between different states. Both are taken to be significantly faster than the motion of the classical oscillators. The thermal scattering is constructed such that the system returns to thermal equilibrium with a bath which is kept at the original temperature of the system.

From an electronic point of view, the displacements of the ligands around the metal site lead to an effective on-site energy. The distortion around the site $\mathbf{R}$ is given by

$$\begin{aligned} D_{\mathbf{R}} &= \frac{1}{4} \sum_{\delta} d_{\mathbf{R}+\frac{1}{2}\delta} \\ &= \frac{1}{4} (d_{\mathbf{R}+\frac{1}{2}\mathbf{e}_x} + d_{\mathbf{R}+\frac{1}{2}\mathbf{e}_y} - d_{\mathbf{R}-\frac{1}{2}\mathbf{e}_x} - d_{\mathbf{R}-\frac{1}{2}\mathbf{e}_y}). \end{aligned} \quad (5)$$

At a particular time, the electrons experience the effective Hamiltonian

$$H = - \sum_{\mathbf{R}\delta} t c_{\mathbf{R}+\delta}^{\dagger} c_{\mathbf{R}} - \sum_{\mathbf{R}} A_{\mathbf{R}} n_{\mathbf{R}}. \quad (6)$$

with an on-site energy $A_{\mathbf{R}} = 4\lambda D_{\mathbf{R}}$. In the ordered system, the on-site energies are given by $A_{\mathbf{R}} = (-1)^{n_x+n_y} A_o$, with $A_o = |A_{\mathbf{R}}|$ for the ordered system. In order to study thermodynamic effects, a large system size is needed and simplifications of the electronic system are necessary. To understand the physics underlying the approximations, let us consider a single metal

site surrounded by four neighboring metal atoms in the charge-ordered state. If the ligands are displaced away from the central site, the on-site energy is $-A_o$ and the surrounding sites have an energy A_o . In bra-ket notation, the single-particle wavefunctions can be written as $|\psi\rangle = \cos\theta|\mathbf{R}\rangle + \frac{1}{\sqrt{2}}\sin\theta\sum_{\delta}|\mathbf{R}+\delta\rangle$, where $|\mathbf{R}\rangle$ denotes an orbital on site $\mathbf{R}$ and $\delta = \pm\mathbf{e}_x, \pm\mathbf{e}_y$. The angle θ is given by $\theta = \frac{1}{2}\arctan\sqrt{2}t/A_o$. The charge density on the central site is given by $n = \cos^2\theta$. To simplify the system, we take the hopping integrals much smaller than the on-site energies ($t \ll A_o$). In that limit, $n \rightarrow 1$. The energies of the (anti)bonding states $\pm\sqrt{A_o^2 + 2t^2} \cong \pm A_o$ and the charge densities are then mainly determined by the on-site energies. A small displacement away/towards the central metal site causes the charge to be located on the central/neighboring sites. A second point to notice is that when neighboring sites have a lower on-site energy, the charge density is equally distributed on the four sites around the central site.

This simple picture of the charge distribution still largely holds in the extended system. Let us consider a system in the narrow band limit with $W/A_o = 0.5$ with the bandwidth $W = 8t$. The charge densities are obtained by diagonalizing the Hamiltonian in Eq. (6) on 50×50 lattice and calculating the charge densities at half filling. We now want to see how the charge density on a site changes when the direction of the displacements of the ligands surrounding the site is reversed. Let us look at the site encircled in red in the inset in the lower left of Fig. 1. Initially, this metal site has a low charge density with the displacements of the surrounding ligands towards this site. Changing the direction of one or two neighboring oscillators has little effect on the charge density on the metal site, see the red line in Fig. 1. This can be readily understood by considering the on-site energies. Changing the direction of the displacement of one and two ligands changes the on-site energy to $A_o/2$ and 0, respectively. However, this is still higher than the on-site energy of the neighboring sites ($-A_o/2$ and $-A_o$). In a narrow band system where $t \ll A_o$, this hardly affects the charge densities from the charge-ordered state. We can see a significant increase in charge density after changing the direction of the displacement for three ligands. In that case the on-site energy is $-A_o/2$ and equal to that of three neighboring ions. When changing the direction of four neighboring ligands, the energy of the central site ($-A_o$) is lower than that of the four neighboring sites $-A_o/2$. The increase in charge on the central site comes predominantly from the four neighboring sites.

From Fig. 1, it is clear that in the narrow-band width limit, changing the direction of the displacement of a ligand mainly affects the charge density on the sites neighboring the ligand. The trends in charge density in the narrow-band limit can be rather well described by a model that divides the charge on a site into four. This is indicated by the ‘‘dumbbells’’ in Fig. 2(a) and 2(b). The filled and open circles correspond to a charge of $n/4$ and $(1-n)/4$, respectively. Since the direction only depends

FIG. 1: The Figure shows the effect of a changes in direction of the displacement of the ligands on the charge density. The charge densities are calculated for a two-dimensional tight-binding model with bandwidth W and on-site energies $\pm A_o$ in the charge-ordered state ($W/A_o = 0.5$). The red line shows the charge density on the site encircled in red in the bottom-left inset when the direction, but not the size, is changed of the ligands surrounding the metal site. The arrows in the inset give the direction of the displacements. The darker colors on the metal sites indicate an increase in charge density. The result is shown for 1-4, and 16 flipped ligand oscillators. The blue and purple lines show the charge densities for the metal sites surrounding the central metal site, see bottom-left inset. The markers give the charge densities using the bond-charge model used in the paper.

on the energy difference between two neighboring metal sites, one can view this as an effective molecular bond between two neighboring sites. The vector $S_{\mathbf{R} \pm \frac{1}{2}\delta}$ indicates the direction of the bond charges. We can assign a position vector $\mathbf{R} \pm \frac{1}{2}\delta$ for the direction vector. This is the same position as that of the ligands connecting the metal sites, see Fig. 2(a). The energetically most-favorable direction is determined by the relative on-site energies of the neighboring sites. The two possible directions correspond to bonding and antibonding states, see Fig. 2(a), where the bonding state corresponds to the situation with the highest electron density on the site with the lowest on-site energy. The results for this model are indicated by markers in Fig. 1. In the unperturbed system, this leads to a checkerboard charge order with charges n and $1 - n$, where the total charge is the sum of the four bond charges. Comparison with the numerical results fixes the value of n . Changing the direction of the displacement of one or two oscillators does not affect the charge order. For three flipped oscillators, the

energy of the central metal site and three surrounding neighbors are equal. In that case, there is no preferential direction of the bond charges giving a bond charge of $\frac{1}{8}$. The on-site energy of the fourth neighboring site is still lower. The charge on the central metal site is then $3 \times \frac{1}{8} + \frac{1}{4}(1 - n) = \frac{5}{8} - \frac{n}{4}$, which approaches $\frac{3}{8} = 0.375$ in the limit of $W \rightarrow 0$. For three neighboring sites, one of the molecular bonds is undecided giving a total charge of $\frac{3}{4}n + \frac{1}{8}$ or $\frac{7}{8} = 0.875$ in the narrow-bandwidth limit. The neighboring site where the connecting ligand is not flipped still has a charge of n . These values are close to the numerical ones, see Fig. 1. When the direction of the ligand displacement is flipped for all four neighbors, the charge on the central site is n . The charge on the neighboring sites is $3 \times \frac{1}{4}n + \frac{1}{4}(1 - n) = \frac{1}{4} + \frac{n}{2}$. In the limit $W \rightarrow 0$, this approaches $\frac{3}{4}$. Therefore, each of the neighboring sites contributes $\frac{1}{4}$ of the charge to the central site. This is obviously expected from symmetry and is the underlying reason that dividing the charge into four bond charges provides satisfactory results. Numerically, the charge on the central site is somewhat lower due to band effects, although it approaches 1 in the limit $W \rightarrow 0$. Additionally, the lower charge in the numerical simulation is due to the small size of the region of flipped oscillators. When the region of flipped ligand oscillators is increased the electron density on the central site quickly approaches n in the narrow band limit, see Fig. 1 with 16 flipped ligand oscillators (see corresponding inset for the flipped oscillators).

Therefore, in the limit that the band width is relatively small compared to the on-site energies resulting from the displacement of the ligands, the trends in charge density can be understood by bond charges between neighboring metal sites. We now formalize this model. With the vectors $S_{\mathbf{R} \pm \frac{1}{2}\delta}$ indicating the direction of the bond charges, see Fig. 2(a), the normalized charge on a metal site $\bar{n}_{\mathbf{R}} = n_{\mathbf{R}}/n$, where n is taken the value in the ordered state, can be expressed as

$$\begin{aligned} \bar{n}_{\mathbf{R}} &= \frac{1}{4} \sum_{\delta=\pm e_x, \pm e_y} s_{\delta} S_{\mathbf{R}+\frac{1}{2}\delta} \\ &= \frac{1}{4} (S_{\mathbf{R}+\frac{1}{2}e_x} + S_{\mathbf{R}+\frac{1}{2}e_y} - S_{\mathbf{R}-\frac{1}{2}e_x} - S_{\mathbf{R}-\frac{1}{2}e_y}). \end{aligned} \quad (7)$$

The charge-order melting in this model does not occur due to n going to zero, but due to changes in the direction of the bond charges due to thermal fluctuations. Obviously, above the critical temperature, the time average of $\bar{n}_{\mathbf{R}}$ is zero. Using Eq. (7), the interaction between the electronic charge and the ligands in Eq. (4) can be rewritten as

$$\begin{aligned} H_{\text{el-ph}} &= -\lambda n \sum_{\mathbf{R}\delta} s_{\delta} \left(\sum_{\delta'} s_{\delta'} S_{\mathbf{R}+\frac{1}{2}\delta'} \right) d_{\mathbf{R}+\frac{1}{2}\delta} \\ &= -\lambda n \sum_{\mathbf{R}} \sum_{\delta'=\pm e_x, \pm e_y} D_{\mathbf{R}} S_{\mathbf{R}+\frac{1}{2}\delta'} \end{aligned} \quad (8)$$

using Eq. (5). In this summation, the same molecular

FIG. 2: (a) Schematic figure of the system. The system consists of metal sites (indicated by the large circles) and ligands (small circles) located between the metal sites. The ligands are classical oscillators. The charge is made up of bond charges (indicated as “dumbbells”) with increased charge density (black filled circle) on one side and decreased charge density (open circle) on the opposite side. The bond charge has two states with an energy difference $\varepsilon_{\mathbf{R}+\frac{1}{2}\mathbf{e}_x}$. For the bonding/antibonding states, $S_{\mathbf{R}+\frac{1}{2}\mathbf{e}_x}$, indicating the direction of the charge-transfer, is aligned/opposite to the displacement. (b) The extended system shows a typical checkerboard charge order. The ligands are indicated by the arrows indicating the displacement from the undistorted system. Photoexcitations cause charge transfers between neighboring sites leading to a flipping of the spins. The photoexcitations do not directly affect the displacement of the ligands. (c) The displacement of the ligands around the metal sites at thermal equilibrium at a temperature of 400 K for a system with a critical temperature of 504 K. The shown system is 224×224 sites. The local distortion is shown relative to the $T = 0$ K charge order, $|D_{\mathbf{R}} - (-1)^{n_x+n_y}|/2$, on a color scale from blue (0, no change in charge order) via white (no order) to red (1, opposite charge order). The bar shows the color change on a linear color scale from 0 to 1.

bond occurs twice. We can remove that to give

$$H_{\text{el-ph}} = - \sum_{\mathbf{R}} \sum_{\delta=\mathbf{e}_x, \mathbf{e}_y} \varepsilon_{\mathbf{R}+\frac{1}{2}\delta} S_{\mathbf{R}+\frac{1}{2}\delta}. \quad (9)$$

The bond energy, given by

$$\varepsilon_{\mathbf{R}+\frac{1}{2}\delta} = \lambda n (D_{\mathbf{R}} - D_{\mathbf{R}+\delta}), \quad (10)$$

determines the energy difference between the two different bond states in Fig. 2(a). The value of λn is taken 30 meV. Since, in the narrow-band limit, the energies are mainly determined by the on-site energies, we neglect the term H_{el} in the remainder. In order to prevent domain formation a small long-range force is added to $\varepsilon_{\mathbf{R}+\frac{1}{2}\delta}$; we return to this below.

The charge dynamics of the system are a result the motion of the ligands and the scattering between the two bond states as a result of photoexcitations, schematically indicated in Fig. 2(b), or thermal fluctuations. Let us first look at the charge fluctuations. According to statistical thermodynamics, the relative occupations are determined by the Boltzmann factor $\exp(-\varepsilon_{\mathbf{R}+\frac{1}{2}\mathbf{e}_i}/k_B T)$. The occupations are made time dependent by associating each bond state with a random-walk generator, for details see Appendix A. The random-walk generator mimics thermal scattering processes that lead to a thermal equilibrium. The random-walk generator fluctuates around a certain value which we can take as zero. At a particular time, the random-walk generator produces a value p . If $|p|$ is less/greater than a certain threshold value,

the lowest/highest bond state is occupied, respectively. The random-walk generator is constructed in such a way that the distribution around the origin is Gaussian. The threshold value can be chosen in such a way that the time average of the occupation satisfies the Boltzmann factors at a particular temperature. The thermal scattering between the two states is taken instantaneous. However, note that the oscillators do not immediately follow the change in charge density. Their response is given by the equations of motion for the oscillators. Although this motion is classical, one expects a comparable response for quantum harmonic oscillators. For a quantum oscillator, the behavior would be that a displaced harmonic oscillator. It is well known that a change in the force causing the displacement leads to the creation of a coherent wave packet whose expectation values reproduce the classical motion regardless of the frequency of the oscillation.

For each time step Δt in the calculation, the occupations of the molecular bond states are determined. The direction of the bonds states determines the on-site charges $\bar{n}_{\mathbf{R}}$. These charges exert a force on the ligands via the electrostatic interaction. If the displacement is small compared to the interatomic distance, the force on the ligand is directly proportional to the charge difference between the metal ions neighboring the ligand, see Eq. (4). We can rewrite the force on the ligand in the following form

$$F_{\mathbf{R}+\frac{1}{2}\mathbf{e}_i} = \pm m \omega^2 a_0 \frac{\bar{n}_{\mathbf{R}} - \bar{n}_{\mathbf{R} \pm \mathbf{e}_i}}{2}, \quad (11)$$

where m is the mass of the ligand atom; ω is the angular

frequency of the oscillation. At rest, the force $F_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i}$ causes a displacement of the ligand atom by $a_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i} = \pm\frac{1}{2}a_0(\bar{n}_{\mathbf{R}} - \bar{n}_{\mathbf{R}\pm\mathbf{e}_i})$ which reduces to $a_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i} = \pm a_0$ in the fully charge-ordered state. When the charge densities are fixed, the real displacement $d_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i}$ performs an oscillation around the equilibrium positions $a_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i}$. The oscillation frequency is taken 120 fs corresponding to an energy $\hbar\omega = 34.5$ meV. An additional force $-2\Gamma\dot{d}_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i}$, where $\dot{d}$ is the velocity, causes a damping of the oscillation. The decay time of the oscillation $\Gamma^{-1} = 500$ fs. The motion of the ligands is then described by the differential equation for a damped harmonic oscillator

$$\ddot{d} = -m\omega^2 d - 2\Gamma\dot{d} + F, \quad (12)$$

dropping the subscripts for clarity. Note that F is only constant for the time Δt . This differential equation can be solved analytically giving for the displacement

$$d(t) = e^{-\Gamma t}(d(0) - a) \cos \tilde{\omega} t + \frac{e^{-\Gamma t}}{\tilde{\omega}} [\Gamma(d(0) - a) + \dot{d}(0)] \sin \tilde{\omega} t \quad (13)$$

with the modified angular frequency $\tilde{\omega} = \sqrt{\omega^2 - \Gamma^2}$. The oscillation occurs around the displacement $a = F/(m\omega^2)$. The exact solution is used to describe the motion of the ions between the times that the electron occupations are adjusted for thermal scattering. The initial conditions after the thermal scattering are equal to the displacements and velocities at the end of the previous step.

Figure 2c shows the displacements for a typical system of 224×224 sites, corresponding to just over 100,000 ligand oscillators and bond charges. The calculation is done for a system at a temperature of 400 K. For the chosen parameters the critical temperature is 504 K. The figure is mainly blue indicating areas with charge order equivalent to the charge order at $T = 0$ K ($D_{\mathbf{R}} = (-1)^{n_x+n_y}$). Thermal fluctuations give rise to small regions with no charge order (white) or inverted charge order (red corresponding to the order $D_{\mathbf{R}} = -(-1)^{n_x+n_y}$).

The long-range charge order in the system can be characterized by the following order parameters

$$\Delta = \frac{1}{N} \sum_{\mathbf{R}} D_{\mathbf{R}} e^{i\pi(n_x+n_y)}, \quad (14)$$

$$C = \frac{1}{N} \sum_{\mathbf{R}} \bar{n}_{\mathbf{R}} e^{i\pi(n_x+n_y)}, \quad (15)$$

where N is the number of metal sites. C and Δ measure the charge and local distortions, respectively, at the charge-ordering wavevector (π, π) . Due to the broken symmetry of the charge order, Δ and C can be positive or negative. The quantities Δ^2 and C^2 are accessible experimentally by, for example, x-ray diffraction^{12,15,19–22} and resonant x-ray scattering¹². The dependence of the order parameter Δ^2 as a function of temperature is given in Fig. 3(a). The order parameter Δ becomes zero at the critical temperature of 504 K.

FIG. 3: (a) The distortion order parameter Δ^2 as a function of temperature. (b) Density plot of the minimum value of Δ^2 as a function of initial temperature and fluence of the pump. The fluence is given as the percentage of flipped bond charges. The inset gives the change in color on a linear scale from 0 to 1. (c) Dependence of Δ^2 as a function of time t after the initial pump. The different curves give the dependence on the fluence of the pump for the same initial state at 313 K. (d), Time dependence of Δ^2 for different initial temperatures, but at a fixed fluence.

III. CHARGE ORDER MELTING

In pump-probe type experiments, the system is excited at a particular time ($t = 0$) and relevant quantities are measured by the probe as a function of time. A wide variety of pumps has been utilized either exciting the charge degrees of freedom or the lattice. Here, we induce instantaneous charge excitations by randomly flipping a certain percentage of bond charges, see Fig. 2(b). This corresponds to effective charge transfers between the metal sites. Although this is obviously a simplification of a pump mechanism, the results here demonstrate that the detailed nature of the pump is not an essential ingredient to induce the charge-order melting and that majority of the long-range order disappears after the photoexcitation. Figures 3c and 3d show the time-dependence of the order parameter Δ^2 for a different number of conditions. During the time development the system is connected to a bath kept at the initial temperature. Fig. 3(c) shows the dependence on the fluence of the pulse (expressed as a percentage of bond charges that are flipped during the photoexcitation). The initial state has a temperature of 313 K and $\Delta^2 = 0.94$. We see a continuous development of Δ^2 as a function of time. For all fluences, oscillations corresponding to the period of the damped ligand oscillators ($\sqrt{\omega^2 - \Gamma^2} \cong \omega$) are observed. For small flu-

FIG. 4: (a) The distortion order parameter Δ^2 (solid) and Δ (dashed) for different systems and fluences: 10% (blue) and 12% (red) fluence with a long-range interaction with a maximum strength of 10% of the short-range interaction (initial temperature is 400 K); 12% fluence (black), but with a four times weaker long-range interaction (initial temperature is 348 K). The vertical dotted lines indicate the times for which the real-space charge order is shown in Fig. 5. (b) Density correlation $\rho(\Delta R)$ in the x (or y) direction as a function of the distance ΔR between the sites. A comparison is made between strong (red, $T = 400$ K) and weak (black, $T = 348$ K) long-range forces but with the same fluence of 12%. The density correlations are shown for different times after the photoexcitation (indicated in the Figure).

ences (4 and 8%), the charge-order starts to recover after the first oscillation. For increasing fluences, the recovery times steadily increase. For fluences of 14% and higher, the minimum in Δ^2 is not reached at the first oscillation. For 16%, a complete melting of the charge order ($\Delta^2 = 0$) is obtained. The recovery only occurs at the timescale of picoseconds. For Fig. 3(d), the temperature of the initial state is varied and the fluence is fixed at an excitation of 4% of the bond charges. Obviously, the initial value of Δ^2 is different due to its dependence on temperature. We see a steady increase of the recovery times as a function of temperature. Whereas the initial drops in Δ^2 are comparable, the magnitude of the oscillations decreases for higher temperatures. Figure 3b combines the results for different temperatures and fluences in a density plot of the minimum value of Δ^2 that is reached after photoexcitation. This fluence plot is similar to that of the structural phase transition in vanadium dioxide¹⁶ showing a steady decrease of the critical fluence needed to induce a complete melting as a function of temperature.

The size of the system under consideration here allows us to look at the reaction of the system to the photoexcitation and the underlying nonequilibrium dynamics at a microscopic level. Let us focus on fluences where the minimum value of Δ^2 is close or equal to zero. Comparing the behaviour of Δ^2 for a fluence of 10% and 12%, see Fig. 4(a), does not directly show too much difference. For 12%, the minimum Δ^2 is lower and reaches zero. After reaching the minimum, the order restores to its original value around 4-5 ps. However, the behaviour

of Δ gives a different picture. We see that for 10% fluence the system returns the original charge order, but for 12%, it continuously moves to the broken-symmetry equivalent, *i.e.* the charge order is inverted. We can see this in more detail when looking at the local distortions in real space, see Fig. 5(a) and 5(b). Full videos are available in the Supplemental Materials²⁹. Note that the charge order has two broken-symmetry states, which are displaced from each other by a lattice constant. The blue and red in the color scheme in Fig. 5 refer to the two broken-symmetry states and are both charge ordered. The absence of charge order is indicated by white. Since the photoexcitation only involves the charge degrees of freedom, the distortions directly after the photoexcitation are equal to those just before the excitation, which is shown in Fig. 2(c). At $t = 50$ fs, we see the immediate response to the photoexcitation by the appearance of sites with no charge order (white). Up to 500 fs, the short-range order creates small islands of opposite charge order. The difference between the two fluences is only apparent in the density of the islands. The minimum in Δ^2 occurs around 1000 fs, where a clear dominant charge order appears. For $t > 1$ ps, the system returns to the thermal equilibrium for the dominant charge-ordered state. For a fluence of 12%, the charge order is entirely inverted and the photoexcitation has switched the system between the two different broken-symmetry states. In the calculations, this behaviour happens every time that the fluence exceeds its critical value, *i.e.* for all fluences and temperatures below the critical temperature in the black region in Fig. 3(b). Note that, apart from the coherent oscillations at short timescales, the behaviour of Δ has similarities with the motion of a system in a double-potential well. After the initial photoexcitation, minima in the double-potential well occur at lower values of Δ and the value of Δ decreases towards the new minimum. If the fluence is sufficiently large, the system will overshoot the $\Delta = 0$ value and end up in the broken-symmetry state when the system returns to thermal equilibrium with the bath.

Coherent electronic and structural motion has been observed experimentally in a wide variety of systems^{8-10,14,15,17-19,21,22} and observed via X-ray diffraction and scattering, reflectivity, and angle-resolved photoemission. However, in some cases^{15,20}, coherent oscillations in the diffraction intensity are absent during the photoinduced melting of the charge order. Although the importance of strong lattice oscillations cannot be denied, it is not clear whether coherent motion, *i.e.* the oscillations are in phase, is necessary to obtain charge-order melting. This statement is supported by the fact that the coherent oscillations decrease when the fluence is increased. Therefore, a stronger decrease in the charge-order parameter generally coincides with less coherent motion. In the calculations, coherent motion is not essential for the charge-order melting. The coherent oscillations are present since the displaced harmonic oscillators are released at the same time. Broadening the excitation pulse removes the coherent mo-

FIG. 5: The time dependence of the charge order in real space for different systems and fluences. Full videos are available in the Supplemental Materials. (a) 10% fluence and $T = 400$ K at different times after the photoexcitation (from left to right, times indicates in the Figure and in Fig. 4. (b), *Id*, but for 12% fluence. (c) 12% fluence, $T = 348$ K, but with a four times weaker long-range force. The charge order is shown relative to the $T = 0$ K charge order, $(D_{\mathbf{R}} - (-1)^{n_x+n_y})/2$, on a color scale from blue (no change in charge order) via white (no order) to red (opposite charge order).

tion (not shown), but hardly affects the change in the charge-order parameter. Although, not a necessary condition, the role of coherent motion should not be entirely ruled out. Recent experiments by Beaud *et al.*²² show large coherent motion that leads to a doubling of the frequency. The diffraction intensity can be viewed as $|\Delta_0(t) + A(t)\cos\omega t|^2$, where $\Delta_0(t)$ is the charge-order parameter without coherent motion and $A(t)\cos\omega t$ describes the coherent motion. We can expand this as $\Delta_0^2(t) + 2\Delta_0(t)A(t)\cos\omega t + (A(t)\cos\omega t)^2$. Therefore, when $\Delta_0(t) \gg A(t)$, the second term dominates and the frequency is ω . However, when the charge order is strongly reduced, $\Delta_0(t) \ll A(t)$ and the third term dominates giving a doubling of the frequency. This situation occurs in the experiments of Beaud *et al.*²², but not in the calculations. The role of this coherent motion in the actual melting of the charge order is still unclear. The time in which the melting occurs in the calculations is comparable to experiment in the sense that the largest reduction of the charge-order parameter occurs within the first oscillation period.

In the examples so far, the system also included a relative small long-range force which we take proportional to the order parameter Δ . This additional term is necessary to keep the system homogeneous. The origin of these long-range forces can be strain effects that prefer a homogeneous system with one type of broken-symmetry charge order. This creates an effective energy difference between the bond states of $\varepsilon_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i} = \alpha[D_{\mathbf{R}} - D_{\mathbf{R}\pm\mathbf{e}_i} + 2P(-1)^{n_x+n_y}\Delta]$. The last term increases the energy difference when the state conforms

to the long-range order thereby reducing thermal fluctuations into the higher-lying state. P gives the relative strength of this interaction with respect to the short-range interactions. In the previous calculations, $P = 0.1$. The black line in Fig. 4(a) shows the time dependence of Δ^2 for 12% fluence when the long-range interaction is reduced by a factor four ($P = 0.025$). The initial temperature is 348 K, which has an equal Δ^2 as $P = 0.1$ at 400 K. The initial decrease in Δ^2 is very similar to that for $P = 0.1$. However, the recovery is very slow and even after several picoseconds Δ^2 is still less than 0.1. Figure 5c shows what happens at an atomic level. Initially, there is very little difference between $P = 0.025$ and 0.1 for 12% fluence. However, whereas the system with the stronger long-range order ($P = 0.1$) returns to the (inverted) initial state, the absence of sufficient long-range order for $P = 0.025$ leads to domain formation destroying the long-range order.

Another key aspect for X-ray diffraction and resonant X-ray scattering is the correlation length, *i.e.* how the charge order at different positions in the system is related to each other. The correlation length determines the width of the diffraction peaks. This quantity can be determined by looking at the density correlation function defined as $\rho(\Delta\mathbf{R}) = |(1/N)\sum_{\mathbf{R}} D_{\mathbf{R}}D_{\mathbf{R}+\Delta\mathbf{R}}|$. The density correlation along x (or y) is shown in Fig. 4(b) for several times t after the photoexcitation for long-range order parameters $P = 0.025$ and 0.1. The reduction in the charge-order parameter (for $t < 1$ ps) is almost independent of the long-range order. It is important to note that, although the magnitude of the density cor-

FIG. 6: The Figure compares the difference in response of two systems with the same initially excited charge-order parameter $C^2(0)$ to photoexcitation and heating. Both the charge C^2 (solid) and distortion Δ^2 (dashed) order parameters are shown. The red curves show the photoexcited system at a temperature $T = 313$ K where the value of $C^2(0)$ is reached by photoexciting the system with a particular fluence. The blue curves are for a system where $C^2(0)$ is reached by instantaneously heating the system to a temperature T' , while keeping the bath at T . (a) Comparison between a fluence of 8% and $T' = 423$ K; $C^2(0) = 0.68$. (b) Comparison between a fluence of 15.6% and $T' = 458$ K; $C^2(0) = 0.50$.

relation decreases during the melting, there is no appreciable change in the ΔR dependence for $\Delta R > 10$. This implies that, although the distortion parameter Δ decreases, there is no significant change in correlation length. Experimentally, this means that whereas the intensity of the diffraction peaks decreases, their widths are hardly affected by the decrease in the charge-order parameter. This is the behaviour typically observed in x-ray diffraction or resonant x-ray scattering^{11,15,20,22} and is strongly indicative of nonthermal behaviour. The recovery however tells a different story. For $P = 0.1$, the density correlations recover over the entire system, albeit slightly faster at smaller distances. For weaker long-range interactions ($P = 0.025$), there is a recovery of the short-range correlation, but the long-range correlation approaches zero due to the formation of domains, see Fig. 5(c).

Finally, we address the question whether the excitations induced by the pump correspond to a simple heating of the material. To this end, a comparison is made between a system at temperature $T = 313$ K that is photoexcited to a particular charge-order parameter C^2 and a system that is instantaneously heated to a temperature T' with the same C^2 . In both cases, the bath is kept at $T = 313$ K. The latter situation represents the idea that photoexcitation simply causes a heating of the material. In order to simulate this situation, the instantaneously heated sample is represented by relaxed system obtained at a higher temperature. The results are shown in Fig. 6 for two different fluences (8% and 15.6%). To reproduce the same charge-order parameter $C^2(0)$, the system

needs to be heated to 423 and 458 K, respectively. For the heated systems, we see that both order parameters exponentially approach the expected C^2 and Δ^2 values for T in a few hundred femtoseconds. The situation is different for the photoexcited system. Although the low fluence of 8% approaches the asymptotic values, albeit more slowly than the instantaneously-heated system, see Fig. 6(a), the high fluence almost reduces the charge-order parameter to zero, see Fig. 6(b). The major difference between heating and photoexcitation lies in the response of the lattice. For the heated system, the lattice and charge are in thermal equilibrium and the recovery after instantaneous heating is well-behaved. In the photoexcited system, there is a large difference in effective temperature of the charge and lattice degrees of freedom, leading to the strong response needed for charge-order melting.

IV. CONCLUSION

In summary, charge-order melting was studied for a macroscopic system with local distortions leading to a number of surprising results. Although coherent motion is observed, it does not appear to be crucial for the melting. This manifests itself in the smaller coherent motion for large fluences, which is opposite to what one would expect if the coherent motion was essential. This was also observed experimentally^{17,19}, where it was attributed to destructive interference effects. In some materials, the oscillations are entirely absent²⁰. In fact, widening of the excitation pulse removes the coherent motion, but not the melting. The dominant factor in the charge-order melting is the fluence of the photoexcitations and the resulting strong imbalance between the charge and lattice degrees of freedom. In the system studied, the complete disappearance of the charge order leads to a transition to the broken-symmetry equivalent charge order. No oscillations between the two broken symmetry states could be obtained. In many cases the behaviour of the system can probably be described by a single parameter²². However, such an approach fails to describe the competition between the underlying different degrees of freedom, which are necessary to understand the strongly different responses to photoexcitation and instantaneous heating. The importance of long-range restoring forces necessary to prevent domain formation is also demonstrated. This particularly affects the behaviour of the recovery phase²⁰. Additionally, it is found that the correlation lengths do not dramatically change, which explain the experimental observation that the drop in the X-ray diffraction is not accompanied by an increase in peak width.

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Appendix A: Thermal fluctuations

We want the two bond states to be occupied according to the Boltzmann factor $\exp(-\varepsilon_{\mathbf{R}\pm\frac{1}{2}\mathbf{e}_i}/k_B T)$ with $i = x, y$. We assume that the system is coupled to a bath at a fixed temperature with an infinite heat capacity. Although this might not directly affect the ultrafast melting, where the effects of coupling to the bath are small, it is important for the recovery phase. In a more realistic systems, the charge-ordered state can couple to different types of bath (electronic states and lattice) with different heat capacities. The choice of this bath allows the system to recover to its original state within a reasonable time period. To include the motion of the ligands and to include temperature fluctuations, we want to have a temporal dependence of the occupations. This is achieved by introducing a random-walk generator that has a Gaussian probability around a fixed value. When the random walk is close to the fixed value, the lowest state is occupied. When the random walk exceeds a certain distance from the

fixed value, the state higher in energy becomes populated. The transitions between the two states of the molecular bond charge are due to thermalization processes, such as Coulomb scattering. These processes are significantly faster than the oscillation period of the classical oscillators that follow the changes in charge density according to their classical equations of motion in Eq. (3).

Since the distribution is Gaussian, it is straightforward to ensure that on average Boltzmann statistics are satisfied. In the calculation, the thermal occupation of the states is adjusted every 1 fs. A random walk is generated around a large number P . The walk starts from a random initial value $p_0 = P(1 + \sqrt{s}\mathcal{R}_0)$, where $-1 \leq \mathcal{R}_i \leq 1$ is a random number; $P\sqrt{s}$ is the width of the random walk. The next step in the random walk is given by

$$p_{i+1} = p_i + [2\theta(r_i - |p_i|) - 1]sr_i \quad \text{with} \quad r_i = \sqrt{2}PR_i, \quad (\text{A1})$$

where $0 \leq R_i \leq 1$ is a random number and $\theta(x)$ is a Heaviside step function. The Gaussian can be centered around zero and its width normalized via $\bar{p}_i = (p_i - P)/P\sqrt{s}$. The histogram of the random walk is close to $e^{-2\bar{p}^2}$. For large P , the distribution is almost independent of P . To avoid minor asymmetries in the random walk, the normalized values can be flipped from time to time. There is on the other hand, a dependence on s . A different s does not affect the final distribution, but does change the “thermal fluctuation time”. We can define $T_{\bar{p}}$ as the average time from $\bar{p}_i > \bar{p}$ to $\bar{p}_i < -\bar{p}$ (or vice versa). Note that a smaller value of s or a larger value of $\bar{p}$ gives a larger $T_{\bar{p}}$. For example, for the calculations, $T_{0.8} \cong 400$ fs.

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