Ultrafast Phase Fluctuations in Vanadium Dioxide

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Abstract: Ultrafast pump-probe experiments and a cooperative lattice model indicate the presence of fractal phase fluctuations that can explain the ultrafast electronic and structural response of VO_2.

Here we investigate by theory and experiment the ultrafast response of a prototypical complex material of modern condensed-matter research, namely VO_2, a strongly correlated material with a first-order phase transition from monoclinic/insulator to rutile/metallic at a temperature of $T_{trans} \approx 68°C$. The crystal structure changes from a monoclinic $P2_1/c$ to tetragonal $P4_2/mnm$ (see Fig. 1a) and the resistivity decreases by more than three orders of magnitude. The phase transition enables many technological applications, for example, ultrafast photoelectric switches, thermochromic windows, and ultrasensitive bolometers, but the interplay between the atomic motions and the emerging electrical and optical phenomena remains to be resolved.

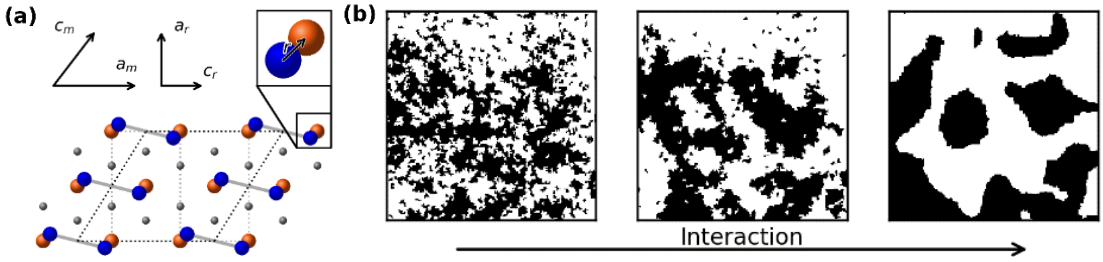

Fig. 1. Crystal structure of VO_2 and simulated fractal domain formation. (a) Crystal structure of VO_2 for low temperature (blue) and high-temperature (orange). **(b)** Left to right, simulated domain patterns for increasing nearest-neighbor interaction.

We simulate the transition using a two-phase lattice model with nearest-neighbor interaction [1]. We obtain a value for the cooperative energy from measured domain structures with a fractal dimension analysis. Figure 1b shows how the simulated domains change shape when cooperativity is increased. With increasing interaction strength, the once jagged and nearly random domain structures (left) begin to consolidate (middle) and eventually form more roundish and well-defined domains (right). The fractal dimension, that is, the scaling behavior of the perimeter-to-area ratio of the individual domains, is therefore a measure of the cooperativity between adjacent unit cells.

A comparison between the fractal dimension of an ensemble of different simulated systems with varying interaction and the fractal dimension obtained from experiments via near-field microscopy and Kelvin probe spectroscopy gives us a nearest-neighbor interaction of 13.8 meV (see Fig. 2a).

Remarkably, this value is close to the thermal energy at room temperature. Consequently, even far below the transition temperature of 68°C, there are lots of spontaneous local phase-flips from the insulating into the metallic phase. These fluctuations that are predicted by our simulations can explain several measured anomalies in VO_2, in particular the low thermal carrier activation energy and the finite conductivity of the insulating phase [1].

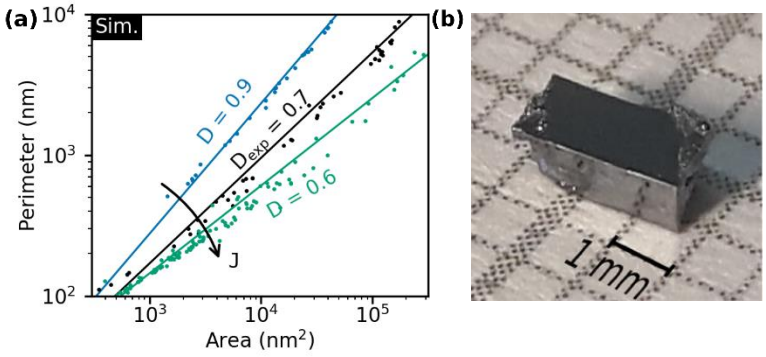

Fig. 2. Fractal dimension analysis and single crystal growth. (a) Simulated perimeter-to-area ratios for increasing interaction strength [1]. **(b)** Single crystal grown by liquid-phase evaporation [2].

Are these fluctuations also relevant for ultrafast dynamics? In the experiment, we measure femtosecond changes of reflectivity in a pump-probe approach. In contrast to many other such experiments, we use here bulk single crystals of VO_2 without any noticeable nanostructure or impurities. Figure 2b shows such a crystal, obtained by thermal decomposition of V_2O_5 at 975 °C under an argon atmosphere at a growth speed limited by liquid-phase diffusion [2]. The pump pulses are obtained from a femtosecond laser (Pharos, Light Conversion) at a center wavelength of 1030 nm at a pulse duration of 300 fs. Mid-infrared probe pulses at 100 fs pulse duration and ~6 µm wavelength, where VO_2 most clearly reveals the insulator-to-metal transition, are generated with a non-collinear optical parametric amplifier and difference frequency generation in a lanthanum gallium silicate (LGS).

The pump-probe results are shown in Fig. 3a. At low excitation fluences (< 5 mJ/cm^2), we see a fast rise in reflectivity that rapidly decays (blue traces). At higher fluences above a threshold (5 mJ/cm^2), the reflectivity does not decay to zero but stabilizes on a certain level (green traces). At even higher fluences (> 7 mJ/cm^2) we see a fast rise, small decay, and then a rise again (yellow curves). The latter phenomenon is slow heat transport from the front to the back of the sample, transforming more and more of the material [3].

Figure 3c shows the height of the initial femtosecond peak at 50 fs (black dots) and the subsequent quasi-equilibration at 5 ps (grey triangles) as a function of the deposited amount of energy. While the long-term data has a threshold at around 5 mJ/cm^2, the initial peak scales linearly with applied laser fluence.

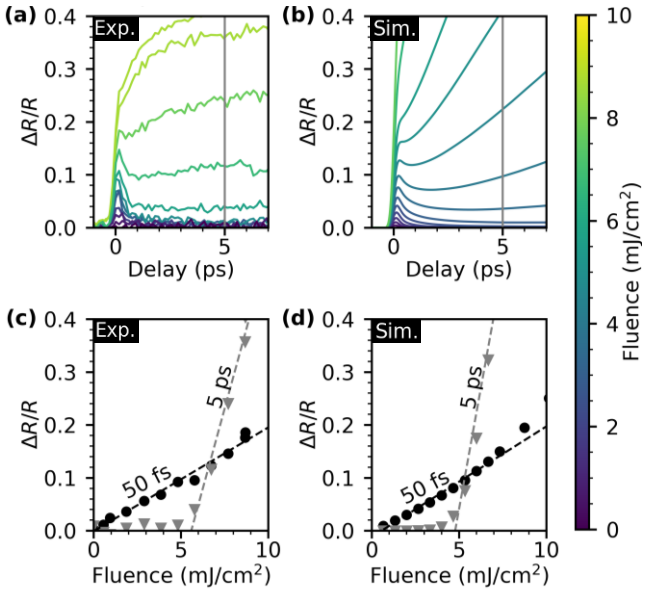

Fig. 3. Ultrafast pump-probe experiments. (a) Time-dependent change in mid-IR reflectivity after ultrafast laser excitation at t = 0 ps. **(b)** Same for our Ising model. **(c)** Scaling behavior of the change in reflectivity 50 fs and 5 ps after laser excitation. **(d)** Same for our lattice model.

We now combine our lattice model with a heat conductivity simulation and use a kinetic Monte Carlo approach to predict the full response in ultrafast experiments. For this purpose, we deposit the energy of each absorbed photon randomly as thermal energy in individual unit cells and then propagate the heat while allowing all individual unit cells to flip according to our lattice model [1]. Despite the simplicity of the approach, the results depicted in Fig. 3b and 3d, show almost the same behavior as the experiment. The remaining difference is a slight static shift of fluence by ~1 mJ/cm^2 due to calibration uncertainties in the experiment. In comparison, a simulation in which the laser pump pulses only homogeneously heat the material without random photon absorption events produces totally different results without any short-time peaks.

We conclude that the pump laser pulses, although fully coherent, are absorbed by the material in a symmetry-breaking way as individual photons that become localized in very small initial domains. Subsequently, these domains quickly grow in a fractal way. If the laser fluence is high enough, the material stabilizes into a macroscopic phase change, but if the fluence is too low, the random initial domains rapidly decay back to the insulating phase. The initial peak in the pump-probe experiments is therefore not produced by hot carriers or related phenomena but simply a consequence of the dynamical and fractal nature of statistical domain formation in a cooperative material at non-zero temperature. Ongoing activities in our laboratory aim at further substantiation of this claim by ultrafast electron microscopy.

[1] D. Kazenwadel†, J. Holder†, P. Nielaba, P. Baum, "Determination of the nearest-neighbor interaction in VO_2 via fractal dimension analysis." Phys. Rev. Res. **5**, 043272 (2023).

[2] D. Kazenwadel†, N. Sprinkart†, R. Hartmann, P. Baum, "Liquid-diffusion-limited growth of vanadium dioxide single crystals." Phys. Rev. Res. **5**, 013028 (2023).

[3] D. Kazenwadel, N. Neathery, S. Prakash, A. Ariando, P. Baum, "Cooling times in femtosecond pump-probe experiments of phase transitions with latent heat." Phys. Rev. Res. **5**, 043077 (2023).