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Photoinduced phase transitions by time-resolved far-infrared spectroscopy in V$_2$O$_3$

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Using time resolved far-infrared spectroscopy, we observe multiple routes for photoinduced phase transitions in V$_2$O$_3$. This includes (i) a photothermal antiferromagnetic to paramagnetic transition and (ii) an incipient strain generated paramagnetic metal to paramagnetic insulator transition which manifests as coherent oscillations in the far-infrared conductivity. The ~100 ps conductivity oscillation results from coherent acoustic phonon modulation of the bandwidth W. Our results indicate that poor metals are particularly amenable to coherent strain control of their electronic properties.

V$_2$O$_3$, a canonical Mott-Hubbard system, is an example of a correlated electron material with an intriguing phase diagram studied thoroughly during last few decades [1–3]. It includes two high temperature phases - paramagnetic insulator and paramagnetic metal - and a low temperature antiferromagnetic insulating phase. Time-integrated optical conductivity measurements have played an important role in elucidating the electronic properties. There is a strong temperature dependence of the spectral weight and a Drude-like quasiparticle peak in the metallic phase disappears in the low (<150K) and high (doped/stressed) temperature insulating phase. The spectral weight is not recovered up to 6eV revealing its strongly correlated nature [4, 5].

Recent studies highlight that while Mott-Hubbard physics provides the backdrop for understanding the metal-insulator transition, subtleties abound [6–11]. Multi-orbital interactions are crucial for a complete understanding and are sensitively influenced by slight static or dynamic changes in the lattice with the consequence that multiple pathways for a phase transition are possible [12]. Time-resolved optical spectroscopy provides a powerful approach to interrogate potential pathways for phase transitions [13–17].

We present time-resolved far-infrared conductivity studies on V$_2$O$_3$ probing phase transition dynamics following photoexcitation. We observe a ~20 ps photoinduced antiferromagnetic insulator (AI) to paramagnetic metal (PM) transition. In addition, in the metallic phase a strain generated incipient PM to paramagnetic insulator (PI) transition manifests as coherent oscillations in the far-infrared conductivity. The ~100 ps conductivity oscillation results from coherent acoustic phonon modulation of the bandwidth W. In the metallic state of V$_2$O$_3$ W is comparable to the on-site Coulomb repulsion U. The observation of this response in V$_2$O$_3$ indicates that poor metals with large U/W ($\gtrsim$1) are amenable to coherent strain control of their electronic properties. From a microscopic perspective, dynamical spectral weight transfer results from coherent strain modification of the orbital interactions of the trigonal split vanadium $t_{2g}$ levels.

Our V$_2$O$_3$ samples are 75 nm thick and are grown on oriented sapphire substrates [18]. The films were confirmed by x-ray diffraction to be single phase V$_2$O$_3$ and have been characterized using optical conductivity measurements [4]. Optical-pump THz-probe measurements were performed with a regenerative amplifier producing 35 fs 3.5 mJ pulses centered at 1.55 eV (800 nm). The THz pulses were generated and detected using electrooptic techniques [16]. All-optical pump-probe measurements were performed using the same experiment to enable direct comparison of photoinduced changes in the
real part of the far-infrared conductivity ($\Delta\sigma_1$) and reflectivity ($\Delta R/R$) at 1.55 eV.

Initial measurements using THz-TDS (i.e. without photoexcitation) were performed to measure the far-infrared conductivity ($\sigma_1$, coherent Drude response) as a function of temperature. Figure 1(a) shows the film transitions from the AI phase to the PM phase at approximately $T_{MIT}=150$K. Below $T_{MIT}$, the far-infrared response vanishes as spectral weight shifts to higher frequencies (see also 100K data in Fig. 1(b)). In the correlated metallic phase above $T_{MIT}$, a maximum conductivity of 850(\Omega\text{cm})^{-1} is obtained at 200K. From 200K to 400K, the conductivity decreases with temperature, consistent with previous work [1, 4, 7].

Figure 1(b) shows the optical conductivity from the far-infrared to 6 eV at 100, 200, and 400 K [4]. Between 400K and 200K there is an increase in the spectral weight below 1 eV. Below $T_{MIT}$ a gap is clearly observed. Trigonal distortion of the tetrahedrally coordinated vanadium ions lifts the degeneracy of the $t_{2g}$ orbitals leading to non-degenerate $a_1g$ and double degenerate $e_g^*$ bands. The spectral features in the 0 - 3 eV range arise from transitions in these bands augmented by strong on-site Coulomb repulsion [4, 7]. Thus, the pump and probe pulses primarily excite and interrogate the vanadium d-orbital manifold.

Figure 2 displays the results of optical-pump terahertz-probe (OPTP) measurements. The incident pump fluence is 1 mJ/cm$^2$, corresponding to an absorbed energy density of $\sim$100 J/cm$^3$. This yields an excitation density of approximately 0.1 electron per unit cell. The initially excited electron distribution relaxes on a picosecond timescale through electron-phonon thermalization leading to an increase in the temperature of the sample on this timescale. Figure 2(a) shows the temporal evolution of $\sigma_1$ (plotted as the change in conductivity, $\Delta\sigma_1(\tau)$) at various initial temperatures ($T_i$) following photoexcitation. As Fig. 2(a) shows, at $T_i=140$K $\sigma_1$ increases with time as the sample evolves toward the metallic state. The conductivity reaches a plateau after $\sim100$ps. On a longer timescale (not shown) heat is transferred to the substrate and $\sigma_1$ recovers to its initial value. For $T_i>140$K, there is a decrease in the magnitude of $\Delta\sigma_1$, reaching a minimum at $\sim185$K and crossing over to a photoinduced decrease in the conductivity. Pronounced $\sim100$ps conductivity oscillations manifest in the metallic state and will be discussed in detail below.

Prior to discussing the origin of the metallic phase conductivity modulation, we consider the transition dynamics from AI to PM. In Fig. 2(a), the magnitude of $\Delta\sigma_1$ decreases with increasing $T_i$ consistent with the notion of heating with $\Delta\sigma \propto 1 - \sigma(T_f)/\sigma(200K)$ where $T_f = T_i + \Delta T$ is the final temperature. $\Delta T$ is the induced temperature change which goes as $\Delta T = \xi / C(T)$ where $\xi$ is the absorbed energy density and $C(T)$ is the specific heat. However, V$_2$O$_3$ has a first order structural phase transition with an associated latent heat (70J/cm$^3$[19]) yielding a sharp decrease in $\Delta T$ near $T_{MIT}$ (see supplementary material for further details). For an absorbed energy density of 100 J/cm$^3$, 70% is needed to overcome the latent heat. This is why at 185K there is virtually no change in the conductivity except for the (nonthermal) oscillatory response. The latent heat plays an important role in determining the fluence threshold and has also been observed in VO$_2$.

A bottleneck in the dynamics associated with the latent heat also manifests in the risetime of the conductivity following photoexcitation as shown in Fig. 2(b). In the AI phase, the risetime is $\sim20$ps which is considerably longer than the time for electron-phonon thermalization. This behavior has been observed in VO$_2$ consistent with nucleation and percolative growth of the metallic phase upon rapid heating into the metallic state [16]. The need for an energy density in excess of the latent heat and percolative kinetics determine the timescale for the final state electronic properties to manifest in a photothermal transition. In the metallic state, this risetime decreases to $3ps (\sim1$ps resolution limited) due to electron phonon relaxation. This is faster than the 20ps risetime observed when starting from the insulating state and highlights the absence of percolative dynamics in the metallic phase.

In addition to thermal effects initiated on a picosecond timescale due to electron-phonon thermalization, there are nonthermal effects. The pronounced oscillations of $\Delta\sigma_1$ that arises in the metallic phase represents such a response. The oscillation period is consistent with a co-
Inhomogeneous excitation due to the finite penetration depth of the pump pulse generates, following rapid electron-phonon thermalization, a non-uniform lattice displacement normal to the sample surface. This lattice displacement induces a longitudinal strain wave resulting in a dielectric discontinuity that propagates at the sound velocity. The resultant \( \Delta R/R \) modulation arises from the probe pulse reflected off the surface interfering with the reflection off of the propagating dielectric discontinuity. The change in reflectivity \( \Delta R \) is described by the expression:

\[
\Delta R(t) = \int_0^{z_0} f(z) \eta(z,t) \, dz
\]

where \( \eta \) is the strain introduced by the lattice displacement, \( z_0 \) is the thickness of the film and \( f(z) \) is the sensitivity function introduced by Thomsen et al [21]. The sensitivity function is fairly complex and includes derivatives of the refractive index with respect to \( \eta \).

For the induced modulation in \( \sigma_1 \), the situation is different in that an interference effect cannot be the origin of the oscillatory signal. The far-infrared probe wavelength (1THz → 300µm) is orders of magnitude greater than the film thickness. Further, with transmission measurements we directly measure \( \sigma_1 \). Thus, the oscillatory part in Fig. 3(a) is described by the following equation:

\[
\Delta \sigma_{osc}(t) = \int_0^{z_0} \frac{\partial \sigma_1}{\partial \eta} \eta(z,t) \, dz
\]

where \( \partial \sigma_1 / \partial \eta \) is the derivative of the conductivity with respect to strain which is of microscopic origin.

For 75nm thin films, the strain waves are not well separated in time. Nonetheless, we are able to identify the oscillatory modes that modulate the conductivity. There are two components labeled as quasi-shear (QS) and surface Rayleigh (SR) in Figure 3. This assignment derives from fits to the data using the frequencies of the acoustic modes in \( V_2O_3 \) as determined from Brillouin scattering studies [27].

In Figure 3(c) we plot \( \Delta \sigma_{osc}(t) \) as the oscillatory conductivity change by subtracting the thermal component from experimental data at 300K. The subtraction is shown in the inset where the red line is a fit with the two temperature model to determine the thermally induced change of \( \sigma_1 \), \( \Delta \sigma_{osc}(t) \) (blue) is fitted to two components consisting of a dominant SR mode with a period of 130ps (8GHz) and a QS mode with a period of 30ps (33GHz) consistent with Ref. [27]. The sum of these two components (green) provides an excellent fit to the data. The contributions of each are comparable though of opposite phase.

The resulting SR and QS mode response results from mode conversion of an initially excited longitudinal strain which likely occurs at the sample-substrate interface. These strain waves correspond to a lattice displacement on the order of \( 10^{-13} \) m, and an induced stress (for a 1 mJ/cm\(^2\) excitation fluence) on the order of 0.5 kbar [10, 19, 27, 28]. This stress yields a \( \Delta \sigma_{1}/\sigma_1 \) of approximately 4% and \( \Delta R/R \) at 1.55 eV of -0.2%.

The conductivity oscillation is consistent with strain induced modulation of the spectral weight where a decrease (increase) in \( \sigma_1 \) corresponds to driving the \( V_2O_3 \) towards (away from) the paramagnetic insulating state. In the PM phase, \( V_2O_3 \) is particularly sensitive to small perturbations since the on-site Coulomb repulsion U is comparable to the electronic bandwidth W, which has an exponential dependence on the atomic displacement.

Figure 4(a) maps the photothermal AI/PM transition (red arrow) and strain-induced PM/PI transition (blue arrow) onto the phase diagram of \( V_2O_3 \) highlighting that
two unique pathways are possible. The AI→PM→PI transition precursor is clearly shown in Fig. 4(a). At an optimally chosen initial temperature (143 K, semiconducting region) and pump fluence (4 mJ/cm²), the peak conductivity reduction at 50ps delay time is purely induced by a tensile strain followed by laser excitation. In Fig.4(c) we perform a detailed study of this peak conductivity reduction (∆σ(t) at 50ps) versus pump fluence and final temperature. This yields three pieces of useful information: i) for the same pump fluence, the higher the final temperature the larger the conductivity decrease. This is in accordance with the slope of the PM/PI phase boundary (Fig. 4(a)). The higher the final temperature, the closer the subsequent strain dynamics would bring the system towards insulating state. ii) At the same final temperature, a larger fluence assures a larger conductivity decreases as this generates a larger amplitude strain wave. iii) In order to achieve a sufficient strain (∼4kbar) to fully drive the PM/PI phase transition would require more than 10 mJ/cm² pump fluence causing irreversible damage to the film (damage threshold is ∼8 mJ/cm²).

Thus, it would be of interest to interrogate the phase transition dynamics in doped samples closer to the transition boundary as indicated in the Fig. 4 (red circle).

In summary, photinduced temperature changes and photoinduced strain provide unique pathways in driving phase transitions in V₂O₅. Further, these mechanisms may provide a powerful approach to tune correlated electron materials to novel metastable phases with order parameters that are not thermally accessible providing a complementary approach to photodoping [29–31].

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