Electrodynamics of the vanadium oxides VO\textsubscript{2} and V\textsubscript{2}O\textsubscript{3}

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The optical/infrared properties of films of vanadium dioxide (VO\textsubscript{2}) and vanadium sesquioxide (V\textsubscript{2}O\textsubscript{3}) have been investigated via ellipsometry and near-normal incidence reflectance measurements from far infrared to ultraviolet frequencies. Significant changes occur in the optical conductivity of both VO\textsubscript{2} and V\textsubscript{2}O\textsubscript{3} across the metal-insulator transitions at least up to (and possibly beyond) 6 eV. We argue that such changes in optical conductivity and electronic spectral weight over a broad frequency range is evidence of the important role of electronic correlations to the metal-insulator transitions in both of these vanadium oxides. We observe a sharp optical transition with possible final state (exciton) effects in the insulating phase of VO\textsubscript{2}. This sharp optical transition occurs between narrow $a_{1g}$ bands that arise from the quasi-one-dimensional chains of vanadium dimers. Electronic correlations in the metallic phases of both VO\textsubscript{2} and V\textsubscript{2}O\textsubscript{3} lead to reduction of the kinetic energy of the charge carriers compared to band theory values, with paramagnetic metallic V\textsubscript{2}O\textsubscript{3} showing evidence of stronger correlations compared to rutile metallic VO\textsubscript{2}.

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I. INTRODUCTION

Vanadium dioxide (VO\textsubscript{2}) and vanadium sesquioxide (V\textsubscript{2}O\textsubscript{3}) have been subjects of intensive experimental and theoretical studies for the past several decades. These systems are considered classical prototypes of materials exhibiting metal-insulator transitions\textsuperscript{2,3} An interesting and intriguing aspect is that the electronic metal-insulator transitions in VO\textsubscript{2} and V\textsubscript{2}O\textsubscript{3} are accompanied by changes in the lattice structure. While there has been progress towards understanding the roles played by electron-electron interactions and the lattice distortion in the metal-insulator transitions, there is no consensus on the mechanism of the metal-insulator transitions, at least in the case of VO\textsubscript{2}. An important difference between the two oxides is that V\textsubscript{2}O\textsubscript{3} is anti-ferromagnetically ordered in the insulating phase whereas the most stable insulating phase (M\textsubscript{1}) of VO\textsubscript{2} does not exhibit magnetic ordering. In M\textsubscript{1} VO\textsubscript{2}, the Peierls distortion leads to dimerization (pairing/charge-ordering) of vanadium ions\textsuperscript{4} thereby preventing magnetic ordering in an otherwise correlated insulator\textsuperscript{5} Another difference between these two oxides is that the nominal valence of vanadium ions in VO\textsubscript{2} is +4 whereas in V\textsubscript{2}O\textsubscript{3} it is +3.

VO\textsubscript{2} undergoes a metal-insulator transition (MIT) at $T \approx 340$ K from a low temperature insulating phase to a high temperature rutile metallic phase. The resistivity decreases by four orders of magnitude across the MIT accompanied by a structural transition from the monoclinic unit cell in the insulator (M\textsubscript{1}) to a tetragonal unit cell in the rutile metal (R). In VO\textsubscript{2}, the vanadium ions are in the +4 valence state, and therefore a single electron resides in the d-orbitals, a scenario supported by theoretical calculations and by recent experiments\textsuperscript{5–8,12}. There has been much controversy on the driving mechanism of the MIT in VO\textsubscript{2}, and over the relative importance of the Peierls scenario within the single particle picture and electronic correlations representing Mott physics\textsuperscript{5,6,7,8,9,11,12,13,14,15,16,17,18,19,20,21}

We have recently demonstrated divergent effective quasiparticle mass in VO\textsubscript{2} as evidence that the MIT is a Mott transition\textsuperscript{22,23}. There is, however, a structural component to the phase transition in the form of a Peierls instability (charge density wave) in the monoclinic insulating (M\textsubscript{1}) phase of VO\textsubscript{2} which leads to unit cell doubling and the formation of vanadium dimers (pairs) along the c-axis (in the rutile basis). The presence of such vanadium chains imparts a quasi-one-dimensional character to what is essentially a three dimensional system. The competing effect of the Peierls instability prevents long-range magnetic ordering in the correlated M\textsubscript{1} phase of VO\textsubscript{2}. Therefore, the M\textsubscript{1} phase of VO\textsubscript{2} should be classified as a Mott insulator that is charge-ordered and not magnetically-ordered\textsuperscript{22}.

V\textsubscript{2}O\textsubscript{3} undergoes a first-order metal-insulator transition at $T \approx 150$ K from a low temperature antiferromagnetic insulating (AFI) phase to a high temperature paramagnetic metallic (PMM) phase. The crystal structure also deforms from monoclinic in the insulating phase to rhombohedral symmetry in the metallic phase. The V-V distance along the c-axis (in hexagonal basis) is larger in the monoclinic insulating phase compared to the rhombohedral metal\textsuperscript{22} While there is debate on the significance of cation-cation covalent bonding along the c-axis to the physics of V\textsubscript{2}O\textsubscript{3}\textsuperscript{22,26,27,28,29,30,31}, the change in crystal structure of V\textsubscript{2}O\textsubscript{3} is not associated with Peierls instability and unit-cell doubling, and magnetic ordering is preserved in the insulating phase. From charge balancing in the chemical formula of V\textsubscript{2}O\textsubscript{3}, the vanadium ions are in the +3 valence state and two electrons are present in the d-orbitals of vanadium. Despite extensive experimental and theoretical effort, there is no consensus on
precisely how the two electrons are distributed within the $t_{2g}$ manifold of the $d$-levels.\textsuperscript{26,27,28,29,30,31,32,33,34,35} There is, however, an agreement that the single-band Hubbard model is inadequate to describe the MIT in V$_2$O$_3$ given the complex multi-orbital character of this material. The experimental results reported here provide further constraints on the intrinsic electronic structure of the PMM and AFI phases of V$_2$O$_3$.

Given that both of these oxides of vanadium exhibit metal-insulator transitions that are accompanied by changes in lattice structure, it is important to understand, on the same footing, their optical properties across the phase transition. A comprehensive study of the optical properties of VO$_2$ and V$_2$O$_3$ will help us gain insight into how charge-ordering in insulating VO$_2$ and magnetic ordering in insulating V$_2$O$_3$ influence the electrodynamics of their respective insulating phases and the neighboring metallic phases. There have been several previous studies that have addressed the optical properties of VO$_2$ and/or V$_2$O$_3$.\textsuperscript{36,37,38,39,40,41,42,43,44} However, none of these studies have reported optical constants of both VO$_2$ and V$_2$O$_3$ over the wide frequency (far infrared to ultraviolet (6 eV)) and temperature ranges that we have been able to investigate in this work.

We find that VO$_2$ and V$_2$O$_3$ are correlated materials in which the important energy scale is the Hubbard intra-atomic Coulomb repulsion energy $U$ leading to changes in optical conductivity and spectral weight at least up to 6 eV. We find that $M_1$ VO$_2$, a Mott insulator that is charge-ordered, exhibits a sharp, distinct feature in the optical conductivity that likely results from the quasi-one-dimensional character of the density of states related to the one-dimensional chains formed by vanadium pairs.

We discuss the possibility that this feature in the optical conductivity of VO$_2$ also has an excitonic origin due to final state effects. Such a distinct feature is absent in the optical conductivity of the Mott insulator V$_2$O$_3$ which is magnetically ordered and lacks the quasi-one-dimensional character associated with charge-ordering. Charge-ordering in insulating VO$_2$ may partially circumvent the effects of the intra-atomic Coulomb repulsion or Hubbard $U$.\textsuperscript{48} Nevertheless, the intra-atomic Coulomb repulsion is necessary for opening the energy gap in $M_1$ VO$_2$ as well as in AFI V$_2$O$_3$. Moreover, electronic correlations dominate charge dynamics in the metallic phases of both VO$_2$ and V$_2$O$_3$, with PMM V$_2$O$_3$ more strongly correlated compared to rutile VO$_2$.

II. EXPERIMENTAL METHODS

Previous optical and infrared studies on V$_2$O$_3$ crystals addressed the issue of changes in spectral weight across the MIT in the energy range up to $\approx$ 1.5 eV.\textsuperscript{39,40,41,42} The availability of high quality V$_2$O$_3$ and VO$_2$ films, and recent advances in broad band ellipsometry at cryogenic and elevated temperatures enable accurate determination of optical constants and changes in spectral weight with temperature over a wide energy (frequency) range.\textsuperscript{45} This is because ellipsometry is a self referencing measurement and the complex ellipsometric constants (real part $\Psi(\omega)$ and imaginary part $\Delta(\omega)$) can be obtained at each incident frequency thereby precluding the need for Kramers-Kronig transformations.\textsuperscript{46} The MIT is literally destructive for pure VO$_2$ and V$_2$O$_3$ crystals which could make accurate measurements in both metallic and insulating states on the same sample very challenging. The VO$_2$ and V$_2$O$_3$ films, on the other hand, do not show signs of deterioration even after going through several cycles across the MIT.\textsuperscript{48}

VO$_2$ films about 100 nm thick were grown on (1012) oriented sapphire (Al$_2$O$_3$) substrates by the sol gel method and the details of growth and characterization are given elsewhere.\textsuperscript{49} Films of V$_2$O$_3$ are 75 nm thick and are grown on (1010) oriented sapphire substrates. The V$_2$O$_3$ films are obtained by annealing VO$_2$ films at 600°C for 30 minutes in a vacuum chamber where the pressure is maintained in the order of $10^{-6}$ torr.\textsuperscript{50} The VO$_2$ films are grown by the sol-gel method on (1010) oriented sapphire substrates\textsuperscript{49} and were used as the starting material in order to obtain crystalline V$_2$O$_3$ films. The films were confirmed by X-ray diffraction to be single phase V$_2$O$_3$. The resistivity of the V$_2$O$_3$ films shows a decrease of more than four orders of magnitude in the metallic phase compared to the insulating phase with $T_c$ = 150 K at the midpoint of the MIT (in the heating cycle) in good agreement with previous reports.\textsuperscript{51} Although the VO$_2$ and V$_2$O$_3$ films are polycrystalline, the MIT characteristics closely resemble properties of bulk samples.\textsuperscript{49,50,51}

The optical constants of the VO$_2$ films were obtained from ellipsometric data (50 meV - 6 eV) and near-normal incidence reflectance data (5 - 80 meV) in the insulating and metallic states. The optical constants of V$_2$O$_3$ films were obtained from a combination of ellipsometric measurements and near-normal incidence reflectance, with ellipsometric data covering most of the frequency range. Ellipsometric data was obtained from 0.6 - 6 eV for $T_c$ = 100 - 400 K, and from 50 meV - 0.7 eV for $T_c$ = 300 - 400 K. Reflectance data was obtained from 50 meV to 0.7 eV from $T_c$ = 100 - 300 K, and from 6 - 80 meV in the temperature range $T_c$ = 100 - 400 K. Unlike previous optical studies on single crystals, the VO$_2$ and V$_2$O$_3$ films were not subject to surface treatment (polishing etc.) which could affect the spectra in the visible-ultraviolet spectral range. Therefore the optical constants are those of the pristine as-grown films.

The real and imaginary parts of the ellipsometric constants of the VO$_2$ and V$_2$O$_3$ films on sapphire substrates were measured for two angles of incidence (60° and 75°). The complex optical constants (and subsequently the complex conductivities) of VO$_2$ and V$_2$O$_3$ were obtained via the analysis of a two-layer model of a film layer on an infinitely thick substrate. The latter aspect of the model is valid for a substrate with rough back-surface which prevents coherent back-reflections.\textsuperscript{47,52} Details of the el-
of VO$_2$ plotted as a function of photon energy for the $M_1$ insulating phase ($T = 295$ K) and the rutile metallic phase ($T = 360$ K). The labels in upper and lower case letters refer to features in $\sigma_1(\omega)$ in the insulating phase and metallic phase respectively. The dashed curves represent the optical transitions that contribute to features “A”, “B”, and “C” in $\sigma_1(\omega)$ in the insulating phase (see text for details). (b) The spectral weight SW(\omega) is plotted as a function of photon energy for the insulating and rutile metallic phases of VO$_2$. The spectral weight is also plotted in units of energy $K(\omega)$ defined in eq. 2.

The complex optical constants of the bare sapphire substrate have been obtained via ellipsometric, near-normal incidence reflectance and normal-incidence transmission measurements and were incorporated into the model. The absolute near-normal incidence reflectance measurements on VO$_2$ and V$_2$O$_3$ films were performed using Drude, Lorentzian and Tauc-Lorentzian oscillators. The complex optical constants of the bare sapphire substrate have been obtained via ellipsometric, near-normal incidence reflectance and normal-incidence transmission measurements and were incorporated into the model. The absolute near-normal incidence reflectance measurements on VO$_2$ and V$_2$O$_3$ films were performed using in-situ evaporated gold film as a reference. The reflectance data was analyzed together with ellipsometric data using the same two-layer model as described previously. The contributions of VO$_2$ and V$_2$O$_3$ phonons to the optical constants in the spectral range $\approx 20$-100 meV were modelled by Lorentzian oscillators. Subsequently, these phonon contributions were subtracted and only the electronic contribution to the optical constants of VO$_2$ and V$_2$O$_3$ is presented and analyzed in this work. We note that the spectral weight of the VO$_2$ and V$_2$O$_3$ phonons is negligibly small compared to the electronic spectral weight, and therefore we will not be concerned with the phonon spectral weight in this work.$^{54}$

**III. RESULTS ON VO$_2$**

In Fig. 1, we plot the real part of the optical conductivity $\sigma_1(\omega)$ of the $M_1$ insulating phase ($T = 295$ K) and rutile metallic phase ($T = 360$ K) of VO$_2$ film. The features in $\sigma_1(\omega)$ of the insulating and metallic phases will be explained within the model of energy levels shown in Fig. 2. According to band theory calculations and photoemission data,$^{5,6,9,38,55}$ the O$_{2p}$ bands lie between 2 eV and 8 eV below the Fermi energy in both the insulating and metallic phases. Also, within band theory calculations, the crystal field splits the degenerate $d$-orbitals into

**FIG. 2: Energy level diagrams for the monoclinic insulating ($M_1$) phase and rutile metallic ($R$) phase of VO$_2$ showing the relevant vanadium and oxygen energy levels and optical transition energies. $E_F$ denotes the Fermi level. The energy level diagram in the $M_1$ phase is based on the results of this work and refs.$^{5,6,9,38}$ and includes the effect of $U$ on the $t_{2g}$ bands. The energy level diagram of the rutile metal is based on this work as well as band theory calculations that give the relative separation between the $t_{2g}$ ($a_{1g}$, $e_g^s$), $e_g^e$ and O$_{2p}$ bands.$^{54}$ However, the effect of $U$ on the $t_{2g}$ bands in the rutile metal is not explicitly included in band theory calculations and may lead to a Hubbard splitting of the $a_{1g}$ band.$^{54}$ In this case, the feature “r” in Fig. 1(b) may alternatively arise from an optical transition between the lower and upper Hubbard bands.**

**FIG. 1: (color online): (a) Real part of the conductivity $\sigma_1(\omega)$ of VO$_2$ plotted as a function of photon energy for the $M_1$ insulating phase ($T = 295$ K) and the rutile metallic phase ($T = 360$ K). The labels in upper and lower case letters refer to features in $\sigma_1(\omega)$ in the insulating phase and metallic phase respectively. The dashed curves represent the optical transitions that contribute to features “A”, “B”, and “C” in $\sigma_1(\omega)$ in the insulating phase (see text for details). (b) The spectral weight SW(\omega) is plotted as a function of photon energy for the insulating and rutile metallic phases of VO$_2$. The spectral weight is also plotted in units of energy $K(\omega)$ defined in eq. 2.**
\( t_{2g} \) bands and \( e_{g}^{\pi} \) bands. The former are lower in energy and contain the single \( d \)-electron. The \( t_{2g} \) bands are further split into an \( a_{1g} \) band and \( e_{g}^{\pi} \) bands, with the latter centered at higher energy compared to the former. We follow Ref.7 in using the terminology \( a_{1g} \) and \( e_{g}^{\pi} \). The \( a_{1g} \) band further splits into what we call the lower \( a_{1g} \) band and the upper \( a_{1g} \) band in the \( M_{1} \) insulator. In the Mott picture, these can be considered as lower and upper Hubbard bands while in the Peierls model, these are the bonding and anti-bonding bands respectively.\(^7\)\(^4\)

The energy gap of 0.6 eV in the monoclinic (\( M_{1} \)) insulating phase is between the filled \( a_{1g} \) band and the empty \( e_{g}^{\pi} \) band. Peierls physics alone cannot explain this large energy gap as pointed out by Mott.\(^2\) Various LDA calculations repeatedly fail to confirm this large energy gap.\(^2\)\(^6\) The failure of LDA to account for a gap in insulating VO\(_{2}\) has been attributed to the shortcomings of LDA in predicting band gaps correctly.\(^5\) However, an energy gap of correct magnitude does appear once correlation effects (Hubbard \( U \)) are taken into account.\(^7\)\(^4\)\(^5\)

In the rutile metal, the energy gap collapses and the Fermi level crosses partially filled \( a_{1g} \) and \( e_{g}^{\pi} \) bands (see Fig. 2).\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)

We attempt to explain the various features in the optical spectra of VO\(_{2}\) (and subsequently of \( V_{2}O_{3} \)) by comparing our data to previous theoretical and experimental results. Peaks at finite energies in the optical conductivity occur when there are direct optical transitions between filled and empty bands in a solid. More precisely, the interband optical transitions are governed by the dipole transition matrix elements and peaks in the joint density of (filled and empty) states. The hump feature in Fig. 1A labelled “A” at 1.4 eV is due to optical transitions from the filled lower \( a_{1g} \) band to the empty \( e_{g}^{\pi} \) bands across an optical gap of \( \approx 0.5 \) eV. It is inappropriate to attribute peak “B” at 2.5 eV to transitions from the narrow lower filled \( a_{1g} \) band to the narrow upper empty \( a_{1g} \) band. Peak “C” at 3.2 eV is due to transitions from the filled \( O_{2p} \) bands and empty \( e_{g}^{\pi} \) bands. We do not observe any obvious signs of optical transitions from the \( O_{2p} \) bands to the empty \( a_{1g} \) band which are expected at \( \approx 4.7 \) eV, and this is likely due to diminished overlap between the \( a_{1g} \) and \( O_{2p} \) orbitals in the insulating state of VO\(_{2}\).

A broad Drude-like feature is observed in the optical conductivity of the rutile metallic phase (labelled “q”). The spectral weight in the Drude-like peak is borrowed from the optical transitions at frequencies higher than 1.3 eV, the energy at which the two solid curves in Fig. 1A cross. We see a weak shoulder “r” at 2.6 eV and a peak “s” at 3.1 eV which we attribute to optical transitions from the \( O_{2p} \) bands to partially filled \( a_{1g} \) and \( e_{g}^{\pi} \) bands respectively. Compared to the monoclinic insulator, the optical transitions from \( O_{2p} \) to the \( a_{1g} \) band become apparent in the rutile metal possibly because of increased overlap between the \( O_{2p} \) and \( a_{1g} \) orbitals. An alternative explanation of the shoulder feature labelled “r” is that it arises from optical transitions between remnants of the lower Hubbard band and upper Hubbard band in the rutile metal. We note that while the lower Hubbard band is seen by photoemission, a feature due to the upper Hubbard band is absent in the X-ray absorption data.\(^2\)

At this point we remark that compared to the broader peaks “A” and “C” in \( \sigma(\omega) \) in the insulating phase, peak “B” is unusually narrow. This is more so in the case of VO\(_{2}\) film grown on (1010) sapphire whose optical conductivity we published in a previous work.\(^2\) In fact, peak “B” is described by a nearly Lorentzian lineshape with half-width of 0.5 eV which is much narrower compared to the corresponding width parameters of the Tauc-Lorentzian oscillators\(^2\)\(^8\) used to describe peaks “A” \((\approx 1.6 \) eV) and “C” \((\approx 1.4 \) eV). The quasi-one-dimensional nature of the V-V chains leads to narrow upper and lower \( a_{1g} \) bands and a sharp optical transition between these bands. In addition, it is possible that peak “B” is excitonic in nature\(^2\)\(^7\) such that the optical transition between the filled and empty \( a_{1g} \) bands is red-shifted by the electron-hole binding energy due to Coulomb attraction. Such an electron-hole pair is described as a charge-transfer exciton\(^2\)\(^8\) whose spatial extent lies somewhere between the Mott-Wannier exciton that is delocalized over several unit cells and the Frenkel exciton that is confined to an atom or molecule. The charge-transfer exciton is likely localized on the vanadium dimer whose V-V separation is 2.65 Å, and thus is more closely related to the Frenkel exciton. The charge-transfer exciton is not present in the rutile metallic phase and this could be due to one or more of the following reasons: merger of the lower and upper \( a_{1g} \) levels, absence of long-range charge-ordering, and screening due to mobile charge carriers.

We make use of the model that is applicable to Mott-Wannier excitons to estimate the binding energy \( (E_{b}) \) of the charge-transfer exciton. It is not obvious if this model is applicable to the charge-transfer exciton in VO\(_{2}\) because of the exciton’s localized character. However, the model appears to provide a reasonable description of charge-transfer excitons in alkali halides and pentacene, for example.\(^2\)\(^9\) The binding energy is given by \( E_{b} = \epsilon e^{2}/\tau_{eh} \) where \( e \) is the electron charge, \( \epsilon \) is the static dielectric constant of VO\(_{2}\) \((\epsilon \approx 20) \) and \( \tau_{eh} \) is the separation between the electron-hole pair in the exciton and is taken to be 2.65 Å which is the V-V distance in the dimer. We hence obtain \( E_{b} \approx 0.27 \) eV. Therefore, we estimate the actual energy separation between the lower and upper \( a_{1g} \) levels to be 2.8 eV. The photoemission and polarized x-ray absorption data suggest that the separation between the \( a_{1g} \) levels is indeed 2.5 - 2.8 eV.\(^2\)\(^9\) It appears that the higher estimate is closer to the picture we present here. The half-width of the \( a_{1g} \) bands in Ref.\(^8\) is \( \approx 1 \) eV. Interband transitions between the lower and upper \( a_{1g} \) energy levels would then be expected to be described by a Lorentzian oscillator with a half-width of at least 1 eV. However, peak “B” is described by a Lorentzian oscillator with a half-width of \( \approx 0.5 \) eV which lends support to the hypothesis that it is excitonic in nature. We note that the assignment of the interband transitions “A”, “C”, “r” and “s”
and “s” are also consistent with the photoemission and x-ray absorption data.\(^2\)

Calculations for the separation of \(a_{1g}\) levels in the V-V dimer start with considering a “hydrogen molecule” model of the dimer.\(^43\) With the intra-atomic Coulomb repulsion \(U\) set to 4.0 eV and the LDA hopping \((t)\) to 0.7 eV, the \(a_{1g}-a_{1g}\) separation is given by \(\Delta_{a_{1g}} = -2t + 4t \sqrt{1 + (U/4t)^2} = 3.48\) eV. This value of \(U\) is required to open an energy gap of the correct magnitude in insulating VO\(_2\). The calculated value for \(\Delta_{a_{1g}}\) is expected to be reduced to 3 eV due to effects not accounted for by the above simple model and discussed in Ref.\(^45\).

The actual position of peak “B” at 2.5 eV is less than the theory value of the \(a_{1g}-a_{1g}\) energy separation. This further supports the notion of its excitonic origin due to final state effects of electron-hole Coulomb attraction that are not accounted for in Ref.\(^45\).

We now discuss the spectral weight changes across the MIT in VO\(_2\). The oscillator strength sum-rule (or \(f\)-sum rule) is a fundamental statement on the conservation of charge in a material. The most generic form employs the integral of the real part of the optical conductivity \(\sigma_1(\omega)\) over all frequencies:

\[
\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi n e^2}{2m_e} \tag{1}
\]

Here, \(n\) is the density of electrons and \(m_e\) is the free electron mass. In reality, however, we study spectral weight changes up to a finite frequency, which in our experiments is 6 eV, and we can comment upon whether or not the \(f\)-sum rule is satisfied in this frequency window. We plot the spectral weight \(SW(\omega) = \int_0^\infty \sigma_1(\omega')d\omega'\) in Fig. 1b for VO\(_2\). The right-hand vertical axis in Fig. 1b shows the spectral weight as an energy \(K(\omega)\) in units of eV which can readily be compared to band theory values. Following Millis et al., the energy \(K(\omega)\) is given by:\(^60\)

\[
K(\omega) = \frac{\hbar a}{e^2} \int_0^\omega \frac{2\hbar}{\pi} \sigma_1(\omega') d\omega' \tag{2}
\]

Here \(a\) is the lattice constant which is taken as \(\approx 3\) Å, the average V-V distance in both VO\(_2\) and V\(_2\)O\(_3\). Also note that \(\hbar/e^2 = 4.1\) kΩ.

Fig. 1b shows that the spectral weight in the broad Drude-like part of the conductivity in the rutile metal is obtained from the loss of spectral weight of the peaks “A”, “B” and “C” in the insulator. In the rutile metal, the \(e^g\) bands and the \(a_{1g}\) band are both partially occupied (see Fig. 2). Therefore, the optical transition (peak “s”) from the O\(_{2p}\) to the \(e^g\) band has reduced spectral weight in the rutile metal compared peak “C” in the insulator. The changes in spectral weight across the MIT extend up to and beyond 6 eV. We note that interband transitions between the filled O\(_{2p}\) and empty \(e^g\) levels may occur above 4 eV but are not expected to change across the MIT. Interband transitions between filled \(t_{2g}\) and empty \(e^g\) are expected at \(\approx 6\) eV (\(U \approx 4\) eV in addition to 2 eV crystal field splitting\(^44\)) and are likely to be modified by the MIT because of the rearrangement of \(t_{2g}\) bands. Thus the changes in optical conductivity and spectral weight that occur above 4 eV across the MIT can be attributed to changes in optical transition probabilities from filled \(t_{2g}\) states to empty \(e^g\) states. The rather large energy scale over which changes in \(SW(\omega)\) are seen across the metal-insulator transition ought to be taken as direct evidence for the predominance of correlation effects, and hence an indication of a Mott transition. Similar large energy scales are involved in spectral weight changes in doped Mott insulators, for example, in the cuprates.\(^55\) We find that the Hubbard parameter \(U\) determines, to a large extent, the energy scale over which \(SW(\omega)\) changes take place across the MIT in VO\(_2\). The Peierls instability within the single-particle scenario alone would result in rearrangement of the \(t_{2g}\) bands within \(\approx 1\) eV of the Fermi energy. Then the scale over which changes in spectral weight occur would be \(\approx 3\) eV and determined by the interband transitions between O\(_{2p}\) and \(t_{2g}\) bands and between \(t_{2g}\) and \(e^g\) bands (without Hubbard \(U\)). Thus changes in \(\sigma_1(\omega)\) and \(SW(\omega)\) that occur well beyond 3 eV provide direct evidence of the importance of correlation effects (Hubbard \(U\)) to the MIT in VO\(_2\).

The energy \(K(\omega)\) associated with the intraband conductivity (the broad Drude-like feature) in VO\(_2\) is \(\approx 0.12\) eV and can be considered as the kinetic energy of delocalized charge carriers.\(^55\) The kinetic energy is determined by setting the intraband cutoff energy at 1.7 eV where the minimum in \(\sigma_1(\omega)\) occurs. The kinetic energy of the delocalized carriers is nearly fifty percent of the band theory value.\(^55,60,64\) Correlations amongst electrons are expected to reduce their kinetic energy compared to that predicted by band theory.\(^59,62\) On the other hand, in the presence of electron-phonon interactions, the ground state wavefunction and hence the kinetic energy of the electrons is essentially that given by band theory.\(^62\) An exception to this occurs in the presence of very strong electron-phonon coupling which can cause a significant reduction in the electronic kinetic energy and likely leads to a polaronic insulating state. However, this scenario is not realized in the rutile phase of VO\(_2\) which is clearly metallic. Therefore, the reduction in kinetic energy of the electrons clearly points to the dominance of correlation effects to the charge dynamics in rutile metallic VO\(_2\). In addition, it was shown in Ref.\(^56\) that the form of the frequency-dependent scattering rate cannot be explained by electron-phonon scattering alone, and that electronic correlations must also influence the charge dynamics. More recently, divergent optical mass was inferred in the metallic nano-scale islands that form in the insulating host at the onset of the MIT in VO\(_2\).\(^2\) This observation is strong evidence for the importance of Mott physics to the insulating and metallic phases in the vicinity of the MIT in VO\(_2\).
IV. RESULTS ON $V_2O_3$

We now turn to the real part of optical conductivity $\sigma_1(\omega)$ of $V_2O_3$ plotted in Fig. 3a. As in VO$_2$, there is rearrangement of $\sigma_1(\omega)$ and $SW(\omega)$ across the MIT. In the insulating phase of $V_2O_3$ at $T = 100$ K, there is an optical gap of $\approx 0.5$ eV followed by interband transitions labelled D to H. Because there are two valence $d$-electrons per vanadium ion in $V_2O_3$, V-V intersite transitions are expected at multiple energies and hence multiple peaks occur in the conductivity data up to 3.5 eV. The energy band diagram for $V_2O_3$ in Fig. 4 gives the relative energy separation between the $O_2p$ and vanadium $t_{2g}$ bands and is a rough guide for the interband transitions and the changes that take place across the MIT. The photoemission data and band structure calculations show that the $O_2p$ bands lie between 3.5 eV and 8.5 eV below the Fermi energy. Then the rise in optical conductivity starting from $\approx 4$ eV is due to interband transitions from the $O_2p$ to the empty $t_{2g}$ orbitals on the vanadium sites. Specifically, the distinct shoulder-like structure “H” in the AFI spectrum can be attributed to such interband transitions. The crystal field splits the vanadium $d$-bands into $e_g$ bands that are centered $\approx 3$ eV above the $t_{2g}$ bands. The lower symmetry of the rhombohedral lattice lifts the degeneracy of the $t_{2g}$ bands, which evolve into non-degenerate $a_{1g}$ and doubly degenerate $e_{g}^\pi$ bands.

We focus our attention on the optical transitions within the vanadium $t_{2g}$ manifold which are better described by considering intersite transitions in real space rather than by appealing to energy bands. This is
because in V$_2$O$_3$, two $d$-electrons are believed to be
distributed in the $e_g^\pi$ and $a_{1g}$ bands in a non-trivial
manner. Lee et al. have discussed, on general physical grounds, the optical excitations
in transition metal oxides with multi-orbital character. However, their classification scheme
does not take into account explicitly the lifting of degeneracy of the $t_{2g}$
bands due to crystal field splitting which may be relevant
for identification of the inter-site transitions in V$_2$O$_3$.

Therefore, assignment of the various interband transitions in both the AFI and PMM phases is
difficult without a quantitative model specific to V$_2$O$_3$. Nevertheless,
relevant physical parameters for V$_2$O$_3$ can be estimated
from our data based on the classification scheme of Lee et al. We note that for two valence electrons in the $t_{2g}$
manifold, the minimum and maximum allowed optical transition energies are given by $U - 3J_H$ and $U + 2J_H$
respectively while assuming the crystal field splitting is
less than the other relevant parameters in the system ($U$, $J_H$ and bandwidth). Here, $U$ is the intra-atomic
Coulomb repulsion and $J_H$ is the Hund's rule exchange energy. Then the lowest energy peak “D” at 1.2 eV in the
AFI spectrum is the optical transition given by $U - 3J_H$ and the energy peak “G” at 3.6 eV is given by $U + 2J_H$.
This gives $U \approx 2.6$ eV and $J_H \approx 0.5$ eV. These numbers are towards the lower end of the spectrum of values
that appear in the extensive literature on V$_2$O$_3$ (for example, see Ref. [30]). It is likely that we have estimated the screened value of $U$ while the unscreened value could be 4.5 eV. We note that in the antiferromagnetic
insulator, each vanadium ion has one nearest neighbor with spin aligned in the same direction and two nearest neighbors with spins anti-aligned. Also, because there are no definitive reports on orbital ordering in AFI, all allowed optical transitions should appear in the spectra of the AFI. We also note here that for reasons given earlier for VO$_2$, the transitions from O$_{2p}$ and $t_{2g}$ bands to the $e_g^\pi$ bands lie close to and beyond the energy cutoff of 6 eV in our experiment. The spectral features due to inter-site transitions between the $t_{2g}$ orbitals of the vanadium ions in V$_2$O$_3$ closely resemble those seen in the Mott insulator YVO$_3$ in which the vanadium ions also have two $d$-electrons in the $t_{2g}$ orbitals. In YVO$_3$, the spectral features between 1 eV and 4 eV were also assigned to inter-site transitions between the $t_{2g}$ orbitals.

From Fig. 3b one can see that there is significant rearrangement of the conductivity spectra across the MIT.
A weak Drude peak labeled “v” and a finite energy mode at 0.5 eV labeled “w” emerge in the metallic phase together with spectral weight enhancement of other interband transitions below 3 eV. In the PMM state, the spectral weight due to the shoulder-like features “G” and “H” decreases. The peaks “E”, “F” and “H” in the AFI spectrum shift downwards by 0.2-0.3 eV and are labelled as “x”, “y” and “z” respectively in the spectra for PMM. This downward shift could be due to the reduction of crystal field splitting between the $a_{1g}$ and $e_g^\pi$ levels. The reduced spectral weight of the “z” feature in PMM compared to “H” feature in AFI is due to the partial occupation of the $a_{1g}$ band in the PMM phase. The decrease in the spectral weight of the $U + 2J_H$ transition (feature “G”) is due to the absence of antiferromagnetic ordering in PMM. Moreover, it appears that ferromagnetic correlations (not ordering) persist in the PMM because of the increase in the optical conductivity (and spectral weight) between 1 and 3 eV compared to the AFI. This is because for ferromagnetic correlations, the optical transitions between $U$ and $U - 3J_H$ will be favored compared to those between $U$ and $U + 2J_H$ [32, 34]. Moreover, orbital switching effects could also contribute to the increased optical conductivity between 1 and 3 eV in the PMM [22].

The Drude peak in the PMM arises from intraband dynamics of coherent quasiparticles of $a_{1g}$ character. This is firmly supported by DMFT calculations in the PMM state [68]. Since the spectral weight of the Drude peak is low, we surmise that the density of coherent quasiparticles is rather low and/or their mass is quite high. Nevertheless, the presence of the Drude peak in metallic V$_2$O$_3$ with dc conductivity below that of the apparent Ioffe-Regel-Mott limit (4000 $\Omega^{-1}$cm$^{-1}$) of metallic transport is remarkable. Next, it appears that the majority of the charge carriers are completely incoherent and reside in the $e_g^\pi$ bands. These likely contribute a broad background to the conductivity and do not give rise to any particular feature in the PMM optical conductivity. The charge dynamics in the dc limit is then dominated by the coherent $a_{1g}$ quasiparticles. The peak “w” can be assigned to intersite transitions between incoherent $e_g^\pi$ carriers and partially occupied coherent $a_{1g}$ orbitals.

In Fig. 4, we see that there is more spectral weight in the metallic phase ($T = 200$K) at low energies compared to the insulating phase ($T = 100$K) and that this extra spectral weight is never fully recovered in the insulating phase up to 6 eV. The additional spectral weight in PMM up to 3 eV is partly borrowed from optical transitions “G” and “H” in AFI. The rest is probably borrowed from higher-lying optical transitions $(> 6$ eV) in the AFI between the O$_{2p}$ bands and the upper Hubbard bands as well as between $e_g^\pi$ and $e_g^\pi$ bands. More interesting is the increase in spectral weight at low energies (up to 3 eV) upon cooling metallic V$_2$O$_3$ from $T = 400$K to $T = 200$K, in accord with previous reports. However, in contrast to previous reports, our data extends up to much higher energies (6 eV) and shows that this increase in spectral weight is only partially accounted for by a corresponding decrease between 3 eV and 6 eV. This is very different from what is expected in cooling a conventional metal that is well-described by band theory. In a conventional metal, the Drude peak narrows as the scattering rate decreases with temperature but the spectral weight is conserved within the bandwidth. In V$_2$O$_3$, the total $t_{2g}$ bandwidth according to band theory is $\approx 2.5$ eV. Therefore, the temperature-driven spectral weight changes in metallic V$_2$O$_3$ that span energies at least up to 6 eV cannot be simply explained within a single-particle picture.
In the PMM phase of $V_2O_3$, the energy $K(\omega)$ does not reach the intra-band value of VO$_2$ (0.12 eV) until about 3 eV of the incident photon energy, well into the region of V-V inter-band transitions. If we assume that only the narrow Drude peak in PMM $V_2O_3$ represents the intra-band part of the energy and spectral weight, then we obtain $K(\omega) \approx 0.012$ eV, the kinetic energy of delocalized carriers, which is nearly six percent of the band value in $V_2O_3$ and significantly less than in VO$_2$. This will place PMM $V_2O_3$ in the strongly correlated limit, with a higher degree of correlations compared to rutile VO$_2$. Therefore, correlation effects are more pronounced in the metallic phase (PMM) near a magnetically-ordered Mott insulator (AFI $V_2O_3$) compared to the rutile metallic $V_2O_3$. The Drude peak to the coherent quasiparticles in $a_{1g}$ and the peak at 0.5 eV to inter-site transitions between the incoherent carriers in $e_{g}^{\pi}$ and coherent empty states of $a_{1g}$ character. This is because the coherent quasiparticles are expected to show a strong temperature dependence compared to the charge carriers in $e_{g}^{\pi}$ that are well above their coherence temperature.

V. SUMMARY AND OUTLOOK

We have investigated the optical constants of VO$_2$ and $V_2O_3$ films over a wide frequency and temperature range. We tracked changes of the optical conductivity $\sigma_1(\omega)$ and spectral weight $SW(\omega)$ across the metal-insulator transitions in both materials. In both VO$_2$ and $V_2O_3$, the changes in $\sigma_1(\omega)$ and $SW(\omega)$ extend up to and beyond 6 eV indicating the importance of electronic correlations to the metal-insulator transitions. From the kinetic energy of charge carriers, we deduce that rutile metallic VO$_2$ and paramagnetic metallic $V_2O_3$ are correlated metals, with metallic $V_2O_3$ showing a higher degree of correlations. Our optics data shows that the energy gaps are nearly the same magnitude in $M_1$ insulating VO$_2$ and anti-ferromagnetic insulating $V_2O_3$ which is interesting given the different lattice structures, magnetic properties and number of d-electrons in the two oxides. While it may be a coincidence that the energy gaps have nearly the same magnitude, it is more likely that the Hubbard $U$ is the common primary factor in determining the energy gap magnitude in both these oxides. Charge ordering of vanadium ions imparts a quasi-one-dimensional character to insulating VO$_2$ resulting in narrow $a_{1g}$ bands and sharp optical transitions between these bands with possible excitonic effects.

When electron-phonon interactions cause metal-insulator transitions to occur, as for example in $V_3O_5$ and Fe$_3$O$_4$, the spectral weight across the phase transitions is conserved on the energy scale of 1 eV. For the MIT in VO$_2$ and $V_2O_3$, the sum rule is not exhausted up to a much higher energy scale of 6 eV, which clearly highlights the important role of electron-electron correlations in the MIT in both these vanadium oxides. Temperature induced changes in optical conductivity and spectral weight are seen over similar large energy scales in other transition metal oxides that are Mott insulators, for example, YVO$_3$, LaVO$_3$, and LaMnO$_3$. Doped Mott insulators like the cuprates also exhibit shift of spectral weight from similar high energies to lower energies upon chemical doping. In this context, our work indicates that Mott physics plays the dominant role in the MIT in VO$_2$ and $V_2O_3$ whereas electron-phonon interactions and the lattice rearrangement play a competing role. Nevertheless, a complete picture of the MIT should take into account the electron-lattice interactions in addition to electron-electron interactions.

Recent work on VO$_2$ provides evidence that the MIT is a Mott transition driven by Brinkman-Rice mass divergence of the quasiparticles. The divergent effective mass occurs in metallic nano-scale puddles that first nucleate in the insulating host in the vicinity of the insulator-to-metal transition. The metallic nano-puddles were observed directly by scanning near-field infrared
FIG. 6: The ellipsometric constants $\Psi(\omega)$ and $\Delta(\omega)$ for the V$_2$O$_3$ film/sapphire substrate system are plotted as a function of photon energy in panels (a) and (b) respectively. The thick dashed gray curves are the data for the AFI phase of V$_2$O$_3$ at $T = 100$ K for two angles of incidence (60° and 75°). The thick solid gray curves are the corresponding data for the PMM phase of V$_2$O$_3$ at $T = 200$ K. The thin solid black curves are fits to the data based on the model described in the section on experimental methods.

FIG. 7: The real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ of the optical constants for the V$_2$O$_3$ film are plotted as a function of photon energy in panels (a) and (b) respectively. The optical constants of V$_2$O$_3$ film plotted in this figure are obtained from modelling of the ellipsometric constants of the film-substrate system displayed in Fig 6a,b. The dashed curves are optical constants of the AFI phase of V$_2$O$_3$ at $T = 100$ K. The solid curves are the optical constants for the PMM phase of V$_2$O$_3$ at $T = 200$ K.

micoscopy. This new data in combination with far-field infrared spectroscopy measurements demonstrated that the effective mass in the metallic nano-puddles of VO$_2$ is significantly enhanced compared to the macroscopic rutile metal at higher temperatures. There is evidence of heavy quasiparticles in metallic V$_2$O$_3$ in the literature although mass divergence in V$_2$O$_3$ has not been explicitly demonstrated. Therefore, V$_2$O$_3$ needs to be studied using the experimental techniques and analytical procedures employed on VO$_2$ in Ref[22] because it is also possible that in V$_2$O$_3$ mass divergence occurs in the vicinity of the MIT where there is a tendency towards phase separation.

In this work, we have displayed evidence of the importance of correlation effects to the metal-insulator transitions in VO$_2$ and V$_2$O$_3$. A corollary is that structural changes in both materials cannot explain the large energy gaps in the insulating phases and the large energy scales that are associated with the metal-insulator transitions. Nevertheless, structural changes cannot be easily explained within Mott physics and likely involve electron-phonon coupling which should be taken into account in any realistic description of the metal-insulator transitions. Moreover, the metal-insulator transition temperatures in both the vanadium oxides we have investigated are an order of magnitude less than the energy gaps in the insulating phases, and there is hardly any satisfactory quantitative explanation for this. However, there are qualitative suggestions emphasizing the importance of the multi-orbital character of these vanadium oxides. Future optical/infrared work on single crystals and/or highly-oriented, epitaxial films of VO$_2$ and V$_2$O$_3$ is required to determine changes in orbital occupation that accompany the metal-insulator transition. Nevertheless, the comprehensive nature of our experiments reported here sets the stage for more in-depth theoretical analysis and specifically computational analysis of the metal-insulator transitions since computational (DMFT and GW) results can be directly compared to optics data.

Note added in proof: A manuscript by L. Baldas-
sarre et al. on infrared measurements on \( \text{V}_2\text{O}_3 \) crystals has been posted recently on the arXiv (arXiv:0710.1247). In this manuscript, the Drude part of the conductivity of paramagnetic metallic \( \text{V}_2\text{O}_3 \) crystals is higher than that of the \( \text{V}_2\text{O}_3 \) films studied in our work.

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APPENDIX

For ellipsometry at cryogenic temperatures, the sample has to be kept in ultra-high vacuum (UHV) to prevent formation of a layer of ice. The ellipsometric measurements (incident photon energies 0.6 - 6 eV) on the \( \text{V}_2\text{O}_3 \) film at low temperatures (100 K \( \leq T \leq 300 \) K) were performed in vacuum of \( \approx 10^{-9} \) torr in a custom-built UHV chamber. The incident and reflected light pass through UHV compatible optical windows. The change in the polarization state of light due to the windows was accounted for via calibration in vacuum using a standard silicon wafer with a 200 Å thick layer of SiO\(_2\).

The ellipsometric constants \( \Psi(\omega) \) and \( \Delta(\omega) \) of the \( \text{V}_2\text{O}_3 \) film on a sapphire substrate are plotted in Fig. 6a,b for the \( \text{V}_2\text{O}_3 \) film in the AFI phase (\( T = 100 \) K) and in the PMM phase (\( T = 200 \) K). The data presented were obtained for two angles of incidence (60° and 75°). Also plotted are fits to the data based on the model described in the section on experimental methods. The optical constants of the \( \text{V}_2\text{O}_3 \) film for the AFI and PMM phases are plotted in Fig. 7a,b and are obtained from modelling of the ellipsometric constants of the film-substrate system.
