Quasiparticle evolution and pseudogap formation in V$_2$O$_3$: An infrared spectroscopy study

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The infrared conductivity of V$_2$O$_3$ is measured in the whole phase diagram. Quasiparticles appear above the Néel temperature $T_N$ and eventually disappear further enhancing the temperature, leading to a pseudogap in the optical spectrum above 425 K. Our calculations demonstrate that this loss of coherence can be explained only if the temperature dependence of lattice parameters is considered. V$_2$O$_3$ is therefore effectively driven from the “metallic” to the “insulating” side of the Mott transition as the temperature is increased.

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Conventional metals are characterized by well-defined long-lived quasiparticles (QPs) that exist up to a coherence temperature $T_{coh}$ of the order of the Fermi temperature. Due to the large value of $T_{coh}$ in comparison with experimentally accessible temperatures, one cannot observe the loss of coherence and of spectral weight expected when $T \approx T_{coh}$. On the other hand, in strongly correlated electron systems, the coherence scale is generally reduced. This is particularly true in the proximity to the Mott transition, where the disappearance of the QPs across $T_{coh}$ (Ref. 1) is therefore expected to be observable. However, a direct experimental observation of this phenomenon is still lacking in what was considered the prototype of the Mott-Hubbard systems: vanadium sesquioxide (V$_2$O$_3$). In particular, there is no characterization, either with optics or photoemission, of what happens when QPs eventually lose their coherence as temperature is increased.

Above 400 K, a badly conducting crossover regime crossing the metal-insulator transition is reached. This analysis is made possible by studying the infrared reflectivity $R(\omega)$ of a high quality single crystal of V$_2$O$_3$ at near-normal incidence. Our work represents a systematic optical study of all the regions (AFI, PM, and CR) of the phase diagram, and it allows us to follow the development of the QPs emerging at $T_N$ from the AFI insulating phase, their evolution into the metallic state for increasing temperature, and their progressive disappearance above $T_{coh}$~425 K, as the system enters the CR.

The extension to high temperature leads us to experimental evidence of the opening of a pseudogap in this material. This is characterized by a strong loss of spectral weight (SW) at low frequency and a downturn in the optical conductivity for $\omega \rightarrow 0$ [note that an analogous downturn has been reported below 300 K for strongly correlated systems such as SrRuO$_3$ (Ref. 8) and, at higher temperatures, for La$_{2-x}$Sr$_x$CuO$_4$ (Ref. 9)].

We also perform calculations with LDA+DMFT (local density approximation combined with dynamical mean-field theory) below and above $T_{coh}$. We find that the key effect behind the pseudogap formation is the temperature dependence of lattice parameters, never considered in previous calculations. The change is small if measured on an absolute scale, but it has a surprising outcome because of the proximity to the Mott transition. At high temperatures, V$_2$O$_3$ lies, in fact, on the “insulating” side of the phase diagram, as if, above $T_{coh}$, one had to bend to the left the blue-crosses straight line in the inset of Fig. 1(a).

The $R(\omega)$ data were collected on a high quality single crystal between 100 and 21 000 cm$^{-1}$ with a Michelson interferometer and for temperatures between 100 and 600 K, completely covering the AFI, PM, and CR phases. Reference was taken on a metallic film (gold or silver, depending on the spectral range) evaporated in situ over the sample surface. The real part of the optical conductivity $\epsilon_r(\omega)$ has been calculated through the Kramers-Kronig transformations. Standard extrapolation procedures were adopted for the insulating or metallic (crossover) phases at low frequency (constant or the Hagen-Rubens extrapolation), while a high frequency tail was merged to our data, as in Ref. 6.

The reflectivity at selected $T$ in the AFI, PM, and CR phases is shown in Fig. 1(a). At $T=100$ K (i.e., well below...
FIG. 1. (Color online) (a) Near-normal incidence reflectivity of V$_2$O$_3$ shown at selected T over the 0–18 000 cm$^{-1}$ range. The phase diagram upon doping with Cr and Ti (Ref. 3) is recalled in the inset. Markers indicate the measurements performed in the present Brief Report. (b) Optical conductivity obtained from the reflectivity in (a), plotted in the same spectral range for the same T. (c) Optical conductivity is shown between 0 and 4000 cm$^{-1}$ to stress the low-energy behavior. Diamonds represent the dc conductivity values as measured by the four-probe resistivity technique. In the inset of (c), $d\sigma /d\omega$ is plotted as a function of frequency up to 2000 cm$^{-1}$.

$T_N$) and at 150 K—not shown—$R(\omega)$ exhibits an insulating behavior with a phonon peak (not discussed here) around 500 cm$^{-1}$. $R(\omega)$ is nearly flat up to about 10 000 cm$^{-1}$ where a weak electronic absorption band appears. For $T>200$ K, instead, the reflectivity is metallic-like (i.e., $R\rightarrow 1$ for $\omega \rightarrow 0$) and decreases over the whole infrared range as temperature increases. Almost no temperature dependence is found above 15 000 cm$^{-1}$ where all the reflectivity curves eventually merge.

A close inspection of Fig. 1(b) reveals in the three regimes different behaviors for $\sigma_1(\omega)$. In the AFI state, $\sigma_1(\omega)$—in good agreement with previous data$^6$—shows a well-defined charge gap in the infrared. The absorption in the gap rises with increasing frequency up to a broad feature in the visible. This is the Mott gap between the Hubbard bands of the strongly correlated AFI.$^{1,15}$ On crossing $T_N$, an abrupt filling of the gap is induced and $\sigma_1(\omega)$ shows, below 1 eV, a metallic absorption due to the appearance of QPs, in good agreement with what is observed for resistivity$^4,5$ and specific heat.$^{14}$ As T is raised, $\sigma_1(\omega)$ presents a strong temperature dependence [see Fig. 1(b)], with a huge transfer of SW from low to high frequency through an isosbestic point at about 6000 cm$^{-1}$. In addition to the metallic term, a broad band is observed in the midinfrared (MIR). This feature was assigned$^6$ to the optical transitions from the Hubbard bands to the states around the Fermi energy.$^{1,15}$

We have also performed four-probe resistivity measurements in the 200–600 K range,$^{16}$ in order to follow the development of the metallic absorption and its evolution with T. The behavior of $\sigma_1(\omega)$ at low frequency has been compared with dc conductivity [diamonds in Fig. 1(c)]. The $\omega \rightarrow 0$ limit of $\sigma_1(\omega)$ and the dc conductivity are in excellent agreement at almost all temperatures. This agreement and the overall decreasing behavior of $\sigma_1(\omega)$ ($d\sigma_1/d\omega<0$), clearly observable for $T<400$ K [see the inset of Fig. 1(c)], suggest the presence of a low-frequency QP contribution between 200 and 400 K. For $T=450$ K, the low frequency $\sigma_1(\omega)$ starts to show a downturn $d\sigma_1/d\omega>0$ in a frequency range that increases with increasing T [inset of Fig. 1(c)]. We associate this change of sign with the disappearance of QPs. On increasing T from 450 to 600 K, the downturn eventually transforms into a pseudogap at low frequency, while the MIR broadens. The pseudogap formation in $\sigma_1(\omega)$ is in agreement with an anomalous enhancement of the dc resistivity of V$_2$O$_3$ when entering the CR.$^{3,4,16}$ Our optical measurements and, in particular, the changes of $\sigma_1(\omega)$ observed at low frequencies between 400 and 450 K [see the inset of Fig. 1(c)] lead to an optical estimate of $T_{c\omega}\approx 425$ K in V$_2$O$_3$.

To quantify the QP term just above $T_N$, and its reduction on increasing T, we have calculated the SW using the restricted $f$ sum-rule$^{12}$ 

$$SW(\Omega,T)=\frac{2nVe}{\Omega}\int_{0}^{\Omega} \sigma_1(\omega,T)d\omega,$$

where $n$ is the mass of carriers, $e$ is the electron charge, and $V_0$ is the volume per unit ion. The temperature behavior of SW is reported for three cutoff energies $\Omega$ in Fig. 2(a), normalized at the 200 K value. SW is nearly constant in the AFI state and shows at $T_N$ a large, discontinuous jump, due to the appearance of QPs. However, on further increasing T, SW($T$) decreases. At the lower cutoff ($\Omega=2000$ cm$^{-1}$), the dramatic loss of SW indicates the loss of coherence mainly of the metallic term, while at the highest $\Omega$ value ($8000$ cm$^{-1}$), the decrease of SW is roughly due to both the QP contribution and the MIR band. Therefore, the loss of SW mainly reflects the lowering of the QP contribution, and, eventually, its disappearance.

As shown in Fig. 2(c), for $200\, K \leq T \leq 550$ K, the SW is proportional to $T^2$, a characteristic behavior of the Fermi liquids. We repeat the analysis introduced for the cuprates,$^{17,18}$ describing the SW as $SW(\Omega,T)=SW(\Omega,0)\left(1-B(\Omega)T^2\right)$, where $B(\Omega)$ depends on the effective QP bandwidth, providing an estimate of the strength of correlation. To single out the free-particle and MIR contributions to the SW, we choose as a cutoff $\Omega=8000$ cm$^{-1}$, where $\sigma(\Omega)$ has a minimum. The value of $B(\Omega)$ does not, however, significantly change if $\Omega$ is chosen up to 15 000 cm$^{-1}$, as far as the discussion in the present Brief Report is concerned. The same value of $B(\Omega)$, within the experimental error, is ob-
FIG. 2. (Color online) Normalized SW for three different cutoffs Ω as a function of T in (a) experiments and in (b) a single-band Hubbard model. The normalization of the theoretical data coincides with the experimental one if D = 1 eV. (c) SW integrated up to 8000 cm⁻¹ as a function of T², showing a linear behavior.

FIG. 3. (Color online) LDA+DMFT optical conductivity for V₂O₃ at two different temperatures. In the inset, the temperature dependence of the ratio c/a is reported (data from Ref. 25). For V₂O₃, the change of c/a observed as a function of T reflects in a dramatic change of the low-frequency optical spectral, i.e., the disappearing of the metallic peak.

obtained by LDA is used to build up a Hamiltonian which is then solved by DMFT using quantum Monte Carlo (QMC) as an impurity solver.

In Fig. 3, we show σ₁(ω) computed with LDA+DMFT at T = 300 and 700 K, respectively, below and above T_{col}. Remarkably, our data are in nice agreement with the experimental result of Fig. 1. In particular, we reproduce the observed high-temperature pseudogap. Had we used the standard input (i.e., the lattice parameters at 300 K) for LDA+DMFT, the optical conductivity at 700 K would have displayed a Drude-like peak rather than a well formed pseudogap as in Fig. 3 (red curve with solid squares). The crucial ingredient of our calculation is the change in lattice parameters of V₂O₃ with increasing temperature, always overlooked in any previous theoretical analysis. Early studies 25 show indeed that the lattice parameters and the atomic positions of undoped V₂O₃ markedly change around 450 K, as opposed to the Cr-doped compound whose lattice parameters are nearly constant in temperature. In particular, above 450 K, the structure of V₂O₃ rapidly approaches that of insulating V₁.₉₆Cr₀.₄₄O₃ (i.e., its LDA bandwidth slightly shrinks) as shown by the ratio c/a between the c- and a-axis lattice constants from Ref. 25 (inset of Fig. 3). Such an effect is taken into account in our calculations in the following way: We fix U = 5 eV (Refs. 21 and 27) and use, at T = 300 K, the corresponding V₂O₃ crystal structure (blue circle in the inset of Fig. 3); for T = 700 K, we use instead V₁.₉₆₂Cr₀.₄₈₃O₃ as an input, which has almost the same lattice constants and a very similar c/a ratio as that of V₂O₃ at the same T (see red box in the inset of Fig. 3).

In conclusion, we measured the optical properties of V₂O₃ in the whole phase diagram. We observed a discontinuous onset of the QP contribution above the MIT and the opening of a pseudogap above T_{coh} = 425 K. This result also calls for a confirmation from high-temperature photoemission experiments, which are still lacking for V₂O₃. LDA+DMFT calculation nicely reproduces our experimental data. However,
the opening of a pseudogap above $T_{coh}$ can only be obtained including the change of the crystallographic parameters with temperature. Atomic or structural disorder does not seem to play a fundamental role here, in contrast to what is expected for doped compounds.\textsuperscript{28} We therefore attribute the pseudogap formation in V$_2$O$_3$ to the temperature dependence of lattice constants, which gives a small shrinking of the LDA bandwidth upon heating. The effect is, however, dramatic, as the change in the lattice parameters effectively drives V$_2$O$_3$ into the insulating side of the Mott transition.

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13While $\sigma_{\text{f}(\omega)}$ in the AFI phase has been previously published, $\mathcal{R}_{\text{f}(\omega)}$ in the same phase has never been reported.


16L. Malavasi et al. (unpublished).


23Note that for the doped Hubbard model, a much smaller variation of SW is obtained (around 10%), since in this case, the metallic behavior is strengthened by the extra charge (Ref. 18).


26We emphasize that our calculation, though much more realistic than the idealized single-band Hubbard model, still involves some approximations. Namely, we do not consider off-diagonal self-energies connecting different bands, and we do not compute the optical dipole matrix elements. Finally, the exchange interactions are approximated through an Ising-like term in order to solve the model through QMC. The latter approximation reduced the tendency to form local spin-1 states, so that the local spin entropy is the same as in the model by C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B 18, 4945 (1978); 18, 4967 (1978); 18, 5001 (1978).
