Metal-Insulator Transition and Lattice Instability of Paramagnetic V$_2$O$_3$

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We determine the electronic structure and phase stability of paramagnetic V$_2$O$_3$ at the Mott-Hubbard metal-insulator phase transition, by employing a combination of an ab initio method for calculating band structures with dynamical mean-field theory. The structural transformation associated with the metal-insulator transition is found to occur upon a slight expansion of the lattice volume by $\sim 1.5\%$, in agreement with experiment. Our results show that the structural change preceeds the metal-insulator transition, implying a complex interplay between electronic and lattice degrees of freedom at the transition. Electronic correlations and full charge self-consistency are found to be crucial for a correct description of the properties of V$_2$O$_3$.

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V$_2$O$_3$ has generally been considered to be the classical example of a material with a Mott-Hubbard metal-insulator phase transition (MIT) [1]. Under ambient conditions, V$_2$O$_3$ is a paramagnetic metal with a corundum crystal structure (space group R$ar{3}$c) [2, 3]. Upon doping with Cr it undergoes a phase transition to a paramagnetic Mott-Hubbard insulator without change of crystal symmetry [4]. The transition from the paramagnetic insulator (PI) to the paramagnetic metal (PM) can also be triggered by doping with Cr, which essentially amounts to the application of a negative pressure. The MIT is intimately linked with an abrupt expansion of the lattice volume by $\frac{\Delta V}{V} \sim 1.3\%$ and a reduction of the c/a lattice parameter ratio by $\sim 1.4\%$ across the MIT, indicating a strong coupling between electronic and lattice degrees of freedom [4]. In spite of intensive research over several decades, an explanation of this mutual influence of electronic structure and phase stability of paramagnetic V$_2$O$_3$ at the MIT is still missing.

A realistic description of V$_2$O$_3$ requires taking into account the interplay of electronic correlations and lattice degrees of freedom on a microscopic level. State-of-the-art methods for the calculation of the band structure, which allow for ab initio computations of the electronic and structural properties, can neither account for the MIT nor the paramagnetic insulating phase of V$_2$O$_3$ [5]. This obstacle can be overcome by employing the LDA/GGA+DMFT approach [6], a combination of band-structure methods in the local-density approximation (LDA) or the generalized-gradient approximation (GGA) with dynamical mean-field theory (DMFT) of strongly correlated electrons [5]. Applications of LDA+DMFT have already provided a good quantitative description of the electronic structure and spectral properties of V$_2$O$_3$ [8, 14]. In particular, it was found that in all phases the V$^{5+}$ ions are in a $S = 1$ spin configuration, with a mixed $(a_{1g}, e_{g}^{\pi})$ and $(e_{g}^{\sigma}, e_{g}^{\pi})$ orbital occupation. These calculations also allowed one to perform a direct comparison of the calculated spectra with, e.g., photoemission, x-ray absorption, and optical conductivity measurements near the metal-insulator transition [8, 14]. The LDA+DMFT results capture all generic aspects of a Mott-Hubbard metal-insulator transition, such as a coherent quasiparticle behavior, formation of the lower- and upper-Hubbard bands, and strong renormalization of the effective electron mass. In addition, these calculations reveal an orbital-selective behavior of the electron coherence and a strong enhancement of the crystal-field splitting between the $a_{1g}$ and $e_{g}^{\pi}$ bands, caused by electron correlations at the MIT [8, 10]. Despite this success the coupling between electronic correlations and lattice structure at the Mott-Hubbard MIT in V$_2$O$_3$ is still poorly understood. We will address this problem in our investigation and thereby shed new light on the long-standing question regarding the origin of the structural changes in the vicinity of the MIT.

In this Letter we employ the GGA+DMFT computational approach [12] to explore the electronic and structural properties of paramagnetic V$_2$O$_3$ across the Mott-Hubbard MIT. In particular, we will explore the structural phase stability of paramagnetic V$_2$O$_3$, i.e., the influence of electronic correlations on the structural transition. We first compute the electronic structure of paramagnetic V$_2$O$_3$ within the nonmagnetic GGA using the plane-wave pseudopotential approach [10]. To investigate the structural stability, we use the atomic positions and the c/a lattice parameter ratio of V$_2$O$_3$ taken from experiment [1]. To this end, we adopt the crystal structure data for paramagnetic metallic V$_2$O$_3$ and insulating (V$_{0.962}$Cr$_{0.038}$)$_2$O$_3$, respectively, and calculate the total energy as a function of volume. In Fig. 1 (inset) we show the results of the nonmagnetic GGA total energy calculations, which agree with previous band structure results [12]. In particular, we find equilibrium lattice constants
\( a = 4.923 \, \text{Å} \) for the PM phase and 4.955 Å for the PI phase of \( \text{V}_2\text{O}_3 \). The calculated bulk moduli are \( B \sim 252 \) GPa for both phases. These results are neither in quantitative nor even in qualitative agreement with experiment. Namely, they give a metallic solution with no structural phase transition between the PM and PI phases. Clearly, standard band-structure techniques cannot explain the properties of paramagnetic \( \text{V}_2\text{O}_3 \) since they do not treat electronic correlations adequately.

Therefore we now compute the electronic structure and phase stability of \( \text{V}_2\text{O}_3 \) using the GGA+DMFT computational scheme [13]. For the partially filled \( V \) \( t_{2g} \) orbitals, which split into \( a_{1g} \) and \( e_{g}^{\pi} \) bands due to a trigonal distortion, we construct a basis of atomic centered symmetry-constrained Wannier functions [17]. To solve the realistic many-body problem within DMFT, we employ the continuous-time hybridization-expansion quantum Monte-Carlo algorithm [18]. The calculations are performed at the temperature \( T \sim 390 \) K, which is below the critical endpoint of \( T_c \sim 458 \) K [19]. We use values of the Coulomb interaction \( U = 5 \) eV and Hund’s exchange \( J = 0.93 \) eV, in accord with the previous theoretical and experimental estimations [8–11]. The \( U \) and \( J \) values are assumed to remain constant across the phase transition [20]. Furthermore we employ the fully-localized double-counting correction, calculated from the self-consistently determined local occupancies, to account for the electronic interactions already described by the GGA.

In Fig. 1 (main panel) we display the calculated variation of the total energy of paramagnetic \( \text{V}_2\text{O}_3 \) as a function of lattice volume. Our results for the equilibrium lattice constant and bulk modulus, which now include the effect of electronic correlations, agree well with experiment [1]. The calculated equilibrium lattice constants are \( a = 5.005 \) Å and 5.035 Å for the PM and PI phases, respectively. The corresponding bulk moduli are \( B = 202 \) GPa and 222 GPa. In agreement with previous studies [8, 10], our results show an orbital-dependence of the electron coherence, with coherent quasiparticle behavior for the \( a_{1g} \) orbital, while the \( e_{g}^{\pi} \) bands remain incoherent, with a large imaginary part of the self-energy at \( T \sim 390 \) K. We also evaluated the spectral function of paramagnetic \( \text{V}_2\text{O}_3 \) (not shown here) and determined the MIT phase boundary. The MIT is found to take place at a positive pressure of \( p_c \sim 125 \) kbar, implying a \( \Delta V \sim 5 \) % reduction of the lattice volume. We find that both the \( a_{1g} \) and the \( e_{g}^{\pi} \) quasiparticle weights remain finite at the MIT, i.e., there is no divergence of the effective electron mass at the transition as it would occur in a Brinkman-Rice picture of the MIT [21]. Thus we conclude that the MIT is driven by a strong enhancement of the \( a_{1g} - e_{g}^{\pi} \) crystal-field splitting caused by electron correlations [8, 10].

The GGA+DMFT results are qualitatively different from those obtained with the nonmagnetic GGA and provide clear evidence for a structural phase transition. However, this transition is found to occur at a critical pressure of \( p_c \sim 186 \) kbar, corresponding to a large (~7 %) reduction of the lattice volume. In addition, the results imply that the PM phase is energetically unfavorable at ambient pressure, i.e., thermodynamically unstable, with a total energy difference w.r.t. to the PI phase of \( \Delta E \equiv E_{\text{PM}} - E_{\text{PI}} \sim 20 \) meV/f.u.. These features are in contrast with experiment. The origin of this discrepancy can be ascribed to the lack of charge self-consistency in the present calculations. Indeed, a strong enhancement of the \( a_{1g} - e_{g}^{\pi} \) crystal-field splitting will cause a substantial redistribution of the charge density and thereby influence the lattice structure due to electron-lattice coupling. All this makes charge self-consistency [22] particularly important at the metal-insulator transition.

For this reason we implemented a fully charge self-consistent GGA+DMFT method [22] within a plane-wave pseudopotential approach to compute the electronic structure and phase stability of \( \text{V}_2\text{O}_3 \). In Fig. 2 we present our results for the total energy for different volumes. The calculated pressure-volume equation of state is shown in Fig. 2 (inset). The PM phase is now found to be thermodynamically stable at ambient pressure, with a total energy difference between the PM and PI phases of \( \Delta E \sim 3 \) meV/f.u. The structural transition takes place upon a slight expansion of the lattice, \( \Delta V \sim 1.5 \) %, at a negative critical pressure of \( p_c \sim -28 \) kbar, in agreement with experiment. The phase transition is accompanied by an abrupt increase of the lattice volume by \( \sim 0.5 \) % and a simultaneous change of the \( c/a \) ratio by \( \sim 1.5 \) %. This result is seen to differ significantly from that obtained with the non-charge-self-consistent GGA+DMFT scheme, according to which the PM phase is thermodynamically unstable at ambient pressure. The calculated equilibrium lattice constants and bulk moduli are now in remarkably good agreement with experiment [4].
particular, we obtain $a = 4.99$ Å and $5.021$ Å for the PM and PI phases, respectively, which is less than 1% larger than the experimental values. The calculated bulk moduli are $B = 219$ GPa and $204$ GPa, respectively. We note that the bulk modulus in the PI phase is somewhat smaller than that in the PM phase, which implies an enhancement of the compressibility at the phase transition. Furthermore, the total-energy calculation results exhibit a weak anomaly near the MIT, which is associated with a divergence of the compressibility, in accordance with previous model calculations. Overall, the electronic structure, the equilibrium lattice constant and structural phase stability of paramagnetic $V_2O_3$ obtained by the fully charge self-consistent GGA+DMFT scheme are in remarkably good agreement with the experimental data. Our calculations clearly demonstrate the crucial importance of electronic correlations and full charge self-consistency to explain the thermodynamic stability of the paramagnetic metal phase of $V_2O_3$.

In addition, we investigated the evolution of the spectral function of paramagnetic $V_2O_3$. In Fig. 3 we present our results obtained with the fully charge self-consistent GGA+DMFT approach for paramagnetic $V_2O_3$ across the MIT. Our calculations show that the $V^{3+}$ ions are in a $S = 1$ spin configuration in all phases, with a predominant occupation of the $e_g^\pi$ bands and substantial admixture of the $a_{1g}$ orbital. The admixture is almost independent of changes of the lattice volume (deviations < 5 %), with a small decrease at the structural transition. Our results for the $(a_{1g}, e_g^\pi)$ orbital occupations at the phase transition are $(0.44, 0.78)$ for the PM phase and $(0.42, 0.79)$ for the PI phase of $V_2O_3$. These findings are in good agreement with previous experimental estimations.

Finally, we calculate the quasiparticle weight employing a polynomial fit of the imaginary part of the self-energy $\text{Im}\Sigma(i\omega_n)$ at the lowest Matsubara frequencies $\omega_n$. It is evaluated as $Z = (1 - \partial \text{Im}\Sigma(\omega)/\partial \omega)^{-1}$ from the slop of the polynomial fit at $\omega = 0$. In Fig. 4 we present our results for the $a_{1g}$ and $e_g^\pi$ quasiparticle weights evaluated for the PI phase. Upon lattice volume expansion, both the $a_{1g}$ and $e_g^\pi$ quasiparticle weights monotonically decrease. Moreover, in the vicinity of the MIT the $a_{1g}$ quasiparticle weight remains finite, while $Z = 0$ for the $e_g^\pi$ orbitals, i.e., $\text{Im}\Sigma(\omega)$ diverges for $\omega \rightarrow 0$. Therefore, we conclude that the electronic effective mass of the $e_g^\pi$ bands diverges at the MIT, in agreement with thermodynamic measurements of $V_2O_3$. We note that this divergence coincides with the drop of the spectral weight for the $a_{1g}$ and $e_g^\pi$ orbitals at the Fermi level shown in Fig. 4.

In conclusion, we employed the GGA+DMFT computational approach to determine the electronic structure and phase stability of paramagnetic $V_2O_3$ across the Mott-Hubbard metal-insulator phase transition. The calculated structural phase stability and spectral properties are in good agreement with experiment. Full charge self-consistency is found to be crucial to obtain the correct equilibrium lattice and electronic structure of $V_2O_3$ at ambient pressure. Upon lattice expansion, a structural phase transition is found to take place at $p_c \sim -28$ kbar, in agreement with experiment. The phase transi-
FIG. 4: (color online) Quasiparticle weight \( Z \) and spectral weight at the Fermi level \( N(\varepsilon_F) \) for the \( a_{1g} \) and \( e_{g}^{\pi} \) orbitals across the MIT in the PI phase of \( \text{V}_2\text{O}_3 \). The MIT itself is indicated by (red) broken line.

The structural transformation is accompanied with an abrupt lattice volume expansion by \( \sim 0.5 \% \) and a simultaneous change of the \( c/a \) lattice parameter ratio by about 1.5 %. Our calculations reveal an orbital-selective renormalization of the \( V t_{2g} \) bands caused by strong electron correlations. The electronic effective mass of the \( e_{g}^{\pi} \) orbitals diverges at the MIT, in accord with a Brinkman-Rice picture of the MIT. However, the \( a_{1g} \) orbital exhibits a finite quasiparticle weight across the MIT. Most importantly we find that the structural transformation is decoupled from the electronic MIT. Our findings highlight the subtle interplay between electronic correlations and lattice stability across the Mott-Hubbard MIT.

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