Defects, disorder and strong electron correlations in orbital degenerate, doped Mott insulators

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We elucidate the effects of defect disorder and e-e interaction on the spectral density of the defect states emerging in the Mott-Hubbard gap of doped transition-metal oxides, such as Y1−xCa3VO7. A soft gap of kinetic origin develops in the defect band and survives defect disorder for e-e interaction strengths comparable to the defect potential and hopping integral values above a doping dependent threshold, otherwise only a pseudogap persists. These two regimes naturally emerge in the statistical distribution of gaps among different defect realizations, which turns out to be of Weibull type. Its shape parameter k determines the exponent of the power-law dependence of the density of states at the chemical potential (k − 1) and hence distinguishes between the soft gap (k ≥ 2) and the pseudogap (k < 2) regimes. Both k and the effective gap scale with the hopping integral and the e-e interaction in a wide doping range. The motion of doped holes is confined by the closest defect potential and the overall spin-orbital structure. Such a generic behavior leads to complex non-hydrogen-like defect states that tend to preserve the underlying C-type spin and G-type orbital order and can be detected and analyzed via scanning tunneling microscopy.

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Defects in semiconductors and insulators determine their transport properties and are responsible for their usefulness for electronics. The hopping between defect states depends on their relative energy and is largely a function of disorder. In case of small hopping amplitudes, the long-range e-e interaction becomes extremely relevant as it modifies substantially the energy of defect states and their occupations. In a seminal work [1, 2], it was shown that a soft gap develops in the density of states (DOS), N(ω) ∝ |ω|κ with exponent κ = d − 1 for system dimension d = 2, 3, in the classical Coulomb glass model: it is known as Coulomb gap [3]. Further theoretical [4–6] and experimental [7] studies confirmed the remarkable success of the strong coupling approach for defects.

We consider defects in a quite different class of compounds: Mott insulators exhibiting a Mott-Hubbard (MH) gap due to short-range e-e interactions [8] that separates the lower Hubbard band (LHB) from the upper Hubbard band (UHB) [9]. Defects in Mott insulators feature many fascinating behaviors [10–16] and are usually thought to lead to only two alternatives: either the MH gap collapses or the defect states inside the gap undergo an Anderson transition, as proposed by Mott [17] for La1−xSr3VO7 and for the high-Tc cuprates. However, why the insulator-to-metal transition occurs in vanadates at much higher doping than in cuprates, although in both systems the MH bands do not disappear with metalization [18, 19], is still not understood. Then, instead from an extended Hubbard model with long-range e-e interactions, which allows us to study the effect of the self-consistent screening of defect potentials, and 3 orbital flavors. It provides a platform for describing the spin-orbital correlations of the perovskite vanadates, such as Y1−xCa3VO7, with active {yz, zx} orbitals at V4+ and coexisting C-type antiferromagnetic (C-AF) spin and G-type alternating orbital (G-AO) order [23].
The motion of a doped hole is bound to the charged Ca defect [Fig. 1(b)] and is further controlled by the underlying spin-orbital structure: it forms a localized spin-orbital polaron [26, 27]. Figure 1(c) displays the associated defect states in the MH gap in the case of a periodic arrangement of defects or, equivalently, of a short-range defect potential [28], and it also reveals the multiplets in the UHB. Due to the CG spin-orbital order, holes tend to form dimer states on specific c-bonds, the active bonds, which results in the formation of a kinetic gap, see Fig. 1(d). Our main goal is to understand whether this kinetic gap survives the potential fluctuations of random defects with long-range Coulomb potentials and which role the screening due to the $t_{2g}$ electrons plays.

Crucial to our analysis are the electron-defect ($V_{im}^D$) and the e-e ($V_{ij}$) interactions, both screened by the background dielectric constant $\epsilon_d$ due to core electrons (no $t_{2g}$ electrons),

$$V_{im}^D = v(R_{im}), \qquad V_{ij} = \eta v(r_{ij}), \qquad v(r) = \frac{e^2}{\epsilon_d r}, \quad (1)$$

where $R_{im}$ and $r_{ij}$ stand for the electronic distances between the V ion at site $i$ and the Ca defect at site $m$ and between two V ions at sites $i$ and $j$, respectively. The typical binding energy of a hole is $V_D = V^D(d) \approx 1 \text{ eV}$ [19], where $d$ is the distance between the defect and its closest V ions and $\epsilon_d \approx 5$.

A hole would propagate along the $c$ axis at $V_D = 0$ [29], similar to an $e_g$ hole in $Y_{2-x}$Ca$_x$BaNiO$_6$ [30].

The Hamiltonian of the doped $Y_{1-x}$Ca$_x$VO$_3$ reads as

$$\mathcal{H}_{t_{2g}} = \sum_{im} V_{im}^D n_i + \sum_{ij} V_{ij} n_i n_j + \mathcal{H}_{CF} + \mathcal{H}_{JT}$$

$$- \sum_{\langle ij \rangle \sigma \alpha} n_{ij}^\sigma (d_{i\sigma \alpha}^\dagger d_{j\sigma \alpha} + H.c.) + \mathcal{H}_{loc}(U, J_H), \quad (2)$$

where $n_i = \sum_{\sigma \alpha} n_{i\sigma \alpha}$ and $n_{i\sigma \alpha} = d_{i\sigma \alpha}^\dagger d_{i\sigma \alpha}$, with orbital flavor $\alpha \in \{a, b, c\}$ standing for $a = yz$, $b = zx$, $c = xy$. The $1^{st}$ two terms in Eq. (2) basically resemble the Coulomb glass model [11, 12] with site energies determined by the (random) positions of defects. The e-e interaction $V_{ij}$ plays a major role in determining the occupation of these states as for $\eta = 1$ the combined defect-hole potential is dipolar [31], while for $\eta = 0$ it is monopolar. $V_{ij}$ is also responsible for the additional screening involving the transitions between the Hubbard bands and the defect states. Further terms in the $1^{st}$ line, $\mathcal{H}_{CF} = -\Delta_c \sum_{i \sigma \alpha} n_{i\sigma \alpha}$ and $\mathcal{H}_{JT}$, denote the crystal-field and Jahn-Teller terms for the $t_{2g}$ electrons [28]. A new dimension of the defect problem arises from the $2^{nd}$ line that includes the nearest-neighbor hopping (the symmetry of $t_{2g}$ orbitals implies that $t_{ij}^\sigma$ is equal to $t$ and different from 0 only for a bond $\langle ij \rangle$ direction different from $\alpha$ [32, 33], and the local Hubbard physics of the triply degenerate $t_{2g}$ electrons, $\mathcal{H}_{loc}(U, J_H)$ [35]. The local Coulomb interactions include intraorbital Hubbard $U$ and Hund’s exchange $J_H$ expressed in the SU(2) invariant form [36]. They are responsible for the multiplets in the UHB for $d$-d charge excitations [Fig. 1(c)].

We solve the Hamiltonian [31] self-consistently employing the unrestricted Hartree-Fock (uHF) approximation [37].

There are two main advantages of the uHF approach we like to emphasize: (i) uHF reproduces the Hubbard bands and the multiplet splitting not only for undoped systems [37], but also in presence of defects [27] and orbital polarization and SU(2) rotation [28]; (ii) the spatial distribution and the occupation of each defect state depends on all other occupied states in presence of disorder and long-range interactions [1]. As a matter of fact, uHF solves this central and complex optimization problem in the most efficient way. The derivation of the uHF equations is standard; more details can be found, for instance, in Refs. [27, 28]. We present results obtained for a cluster of $N_a = 8 \times 8 \times 8$ V ions with periodic boundary conditions, after averaging over $M = 100$ statistically different Ca defect realizations. We use the standard parameters for YVO$_3$, i.e., $U = 4.0 \text{ eV}$, $J_H = 0.6 \text{ eV}$, $\Delta_c = 0.1 \text{ eV}$ [28].

The $2_{\text{spin}} \times 3_{\text{orbital}} \times N_a$ uHF eigenvalues $\epsilon_{s,\lambda}$ obtained for a given defect realization $s$ yield the averaged DOS per V ion,
different defect realizations calls for an overall alignment of the energy scales by means of the different $\mu_x$.

Figure 2 displays the variation of the MH multiplets for different strengths of e-e interaction, encoded by the parameter $\eta$, for doping $x = 2\%$ of random Ca defects (i.e., for 10 defects) [cf. Figs. 1(c) and (d) for a periodic arrangement of defects]. The electronic states close to the defects are pushed by the potential $V_D$ away from the LHB into the MH gap. However, the actual energy distribution of defect states is strongly dependent on the screening of the $e_{2g}$ electrons via the e-e interaction and a soft gap gradually opens up in the DOS on increasing $\eta$. The inset (b) clearly shows the non-monotonous variation of the defect states inside the MH gap on varying the screening. On the large energy scale, two important changes occur when $\eta$ is varied. For $\eta = 0$, the defect potential is unscreened and the interaction with further randomly distributed defects broadens the Hubbard bands. For $\eta = 1$, the screening is instead complete: each defect forms an exciton with a doped hole and the resulting interaction between excitons is dipolar with a tremendous suppression of the effects of disorder and a dramatic narrowing of the Hubbard bands.

To analyze the behavior of the soft gap in $N(\omega)$ without suffering from the unavoidable smearing, we discuss next the averaged integrated DOS, $n(\omega) = \int_{-\infty}^{\infty} d\omega' N(\omega')$, in the vicinity of the Fermi energy and the related plateau [see Figs. 2(c) and (d)]. It is worth noting the following key features in $n(\omega)$: (i) there is an evident gap/plateau for $t = 0.2$ eV (being a typical value for cubic vanadates [32]) and $\eta = 1$, but not for small $t = 0.01$ eV, and (ii) on decreasing the screening $\eta \rightarrow 0$, the gap/plateau disappears even for $t = 0.2$ eV.

In order to establish the statistical behavior of $N(\omega)$ in the limit $M \rightarrow \infty$, we use that $N(\omega)$ is proportional to the probability distribution function $P^*(\omega)$ that a state in a generic defect realization has energy $\omega$ relative to its Fermi energy $\mu_x$. Then, we find that a generic defect realization features a gap of size $E$ with a probability governed by a Weibull probability distribution function,

$$P(E) = \theta(E - \zeta) \frac{k}{\lambda} \left( \frac{E - \zeta}{\lambda} \right)^{k-1} e^{-(E - \zeta)/\lambda},$$

with shape parameter $k$, scale parameter $\lambda$ and location parameter $\zeta$. Accordingly, if $\zeta = 0$, we have $P^*(\omega) = \frac{\omega^{k-1}}{\lambda^k} |\omega|^{k-1}$ and $N(\omega) \propto |\omega|^{k-1}$ both for $|\omega| \ll \lambda$, that is we have a soft gap for $k \geq 2$, a pseudogap for $1 < k < 2$ and no gap for $k = 1$. Instead, if $\zeta > 0$, we have $N(\omega) = 0$ for $|\omega| \leq \zeta$ and $N(\omega) \propto (|\omega| - \zeta)^{k-1}$ for $\zeta < |\omega| \ll \lambda$, that is we have a hard gap. Thus, $P(E)$ results in a robust scheme to determine the behavior of $N(\omega)$ close to the Fermi energy, that is the presence and type of gap in the system. The numerical data obtained for the gaps of $M$ defect realizations for $t = 0.2$ (0.01) eV and $\eta = 0$ and 1 are compared in Figs. 3(a) and (b) to the corresponding statistical least-squares fits to $P(E)$. The fits are indeed excellent in all cases and give systematically $\zeta = 0$.

In Fig. 3(c), we report the $n(\omega)$ curves of Fig. 2(c) successfully reconstructed with the help of $P(E)$. The plateau/gap $\Delta$ present in Fig. 2(c) for $\eta \geq 0.5$ is due to the finiteness of $M$: its statistical value is $\Delta = |\lambda| / \sqrt{M}$ that vanishes for $M \rightarrow \infty$. Figures 3(d) and 3(e) summarize the dependence of $k$ and $\lambda$ on the e-e interaction strength $\eta$ and $t$, respectively. Both $k$ and $\lambda$ increase with increasing e-e interaction $\eta$, see Fig. 3(d). At $t = 0.2$ eV, for $\eta > 0.5$, we have $k > 2$ and, therefore, a soft gap. On the contrary, for $t = 0.01$ eV, $k < 2$ is found for all values of $\eta$: the e-e interaction alone is not sufficient to stabilize a gap and only a pseudogap persists. It is worth noting the almost linear increase of both $k$ and $\lambda$ with increasing $t$ shown at $\eta = 1$ in Fig. 3(e), which justifies calling the soft gap a kinetic gap. We also observe a rather slow, but monotonous, decrease of $\lambda$ on increasing the doping $x$. The most important feature is the non-universality of the exponent $k$ that scales with both $\eta$ and $t$, and is not simply given by the system dimensionality, in contrast to the Coulomb gap in disordered semiconductors [1, 2].

The kinetic gap formation is triggered by the doped holes that do not form symmetric, hydrogen-like, orbitals around the defects. Instead, due to the interplay with the spin-orbital order, they form composite spin-orbital polarons that localize in a symmetry broken form on active bonds. Which of the 4 closest c-bonds of a defect is chosen depends on the interactions with all other defects. To detect and analyze these complex defects, we study in the following the scanning tunneling microscopy (STM) patterns [39, 42] that correspond here to the spatially resolved spin-orbital ($\sigma$) DOS integrated from the

![Figure 3](image-url)
Fermi energy to the applied voltage $V$ for a particular defect realization $s$, $\rho_{\sigma}(x, y, z; V) = |\int_{0}^{V} d\omega \rho_{\sigma}(x, y, z; \omega + \mu_{s})|$. The integrated unoccupied density pattern summed over all spin-orbital degrees of freedom, $\sum_{\sigma} \rho_{\sigma}(x, y, z; V)$, is shown in Fig. 4a for $V = 1.0$ eV. In the lower left corner, we recognize an unoccupied defect state (A) at coordinates $(x, y, z) = (2, 1, z)$ with a finite hole density at vanadium sites $z = 1, 2$ (on the active bond). The asymmetry relative to its closest Ca defect at $(1.5, 1.5, 1.5)$ is evident. The degree of orbital polarization, i.e., increased weight at $z = 2$, is due to the other defects and the Jahn-Teller potential. Fig. 4b shows the occupied density for $V = -0.7$ eV. Close to the same defect at $(1.5, 1.5, 1.5)$, we see two occupied $c$-bonds: one at $(1, 1, 1 & 2)$ with two electrons per site (spectator sites), and another one at $(2, 1, 1 & 2)$ — the active bond (A), with a single hole fluctuating in an asymmetric way along the bond parallel to the $c$ axis. The defect (B) has its hole on a neighbor $y$-plane and we see only spectator sites. (C) and (D) mark a pair of active bonds belonging to three V cubes hosting three defects. More defect states appear at $V = -0.8$ eV [Fig. 4c] that are not well separated from the LHB. Here the complexity of the defect landscape is apparent as well as the interaction of the doped holes with the spin-orbital background.

The landscapes in Figs. 4(d-f) represent the partly occupied spin-orbital densities $\rho_{\sigma}(x, y, z; V)$ of defect states at $V = -0.8$ eV. The red/blue stripe structure for up (down) spins reveals that both the underlying $C$-AF spin order and the $G$-AO order survive the doping by charge defects, in contrast to what happens in high-$T_c$ cuprates where the spin order of the parent compound is destroyed [43, 44]. This supports the findings of the Tokura’s group that $C$-AF/G-AO order is preserved in various doped vanadate systems [19].

Summarizing, we have shown that charged defects in vanadates generate an intrinsic kinetic gap within the Mott-Hubbard gap that survives defect disorder for strong $c$-$e$ interactions implying a strong dielectric screening. The kinetic gap transforms into a soft gap with power-law dependence: $N(\omega) \propto |\omega|^{k-1}$. We have established that the exponent $k$ is non-universal and scales with both the kinetic scale $t$ and the $c$-$e$ interaction strength $\eta$. We suggest that an STM analysis can provide highly valuable microscopic information on the complex non-hydrogen-like states of doped holes, but this remains an experimental challenge.

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