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Gap states in a doped Mott–Hubbard insulator

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Abstract. Static, non-magnetic impurities give rise to gap states in a doped Mott–Hubbard antiferromagnetic insulator. The spectral and spatial features of these gap states are discussed, and it is argued that these gap states are responsible for the observed local-moment behaviour in zinc-doped cuprates.

Keywords. Doped antiferromagnet; gap state; local moment.

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1. Introduction

Doping of static, non-magnetic impurities like zinc, gallium, aluminium into the Cu–O plane of superconducting cuprates has recently been studied quite intensively, aimed partly at exploring the fundamental nature of the superconducting state. One of the very intriguing consequences of doping with these non-magnetic impurities is the observed presence of local moments in the Cu–O plane. This was inferred earlier from the Curie–Weiss behaviour of the magnetic susceptibility [1, 2], and has been recently confirmed in the Y-NMR linewidth studies of doped 1–2–3 systems, as seen in the progressively increasing linewidth of the NMR signal with decreasing temperature [3, 4]. The drastic reduction in T_c upon doping with static, non-magnetic impurities which replace Cu from the Cu–O plane is another remarkable effect and it is believed that the suppression in T_c is due to the magnetic pair-breaking effect. While some correlation between the suppression in T_c and the size of the local moment induced in the Cu–O plane has been found [5] quantitative attempts to ascribe the T_c-reduction to conventional magnetic pair-breaking mechanism range from a several-orders-of-magnitude discrepancy [6] to an order-of-magnitude agreement [4].

A Zn^{++} ion with its filled 3d shell replacing a Cu^{++} ion in $3d^9$ configuration eliminates a Cu spin producing a local spin deficiency in the CuO plane, and hence the local moment produced has been discussed in terms of a spin-hole. Such a view of the system as an antiferromagnet (AF) plus a spin-hole at the impurity site is, however, too simplistic in the context of the recent Y-NMR experiments in which the absolute local moment is probed, and which, in fact, seem to indicate the presence of appreciable local moment on Cu sites neighbouring the zinc dopant sites [4]. Obviously a detailed electronic picture of the doped antiferromagnet would be useful.

In this communication we initiate a study of electronic and magnetic properties of the Mott–Hubbard antiferromagnet doped with static, nonmagnetic impurities in terms of a Hubbard model representation for 3d holes. We model zinc-type dopants by high impurity potentials (V) on the dopant sites, to ensure the absence of any 3d

hole density on these sites. Focussing on the electronic spectral properties, we find that an impurity produces, in addition to the impurity state at energy near V, a localized state within the *Hubbard gap*. For large V this gap state lies very close to one of the band edges (upper/lower band for positive/negative V), and has a wave-function which is localized around the dopant site with appreciable amplitude on nearest-neighbour sites, and which falls-off as a power law at large distances. The electron occupying the localized gap state produces a moment in the Cu–O plane with a Curie-type contribution to the total magnetic susceptibility. Electrons in the Hubbard band and in the impurity states form compensated spin systems and therefore contribute (for $T \ll J$) an essentially temperature-independent term to the magnetic susceptibility.

The specific model we consider is a Hubbard model for 3d holes (with two orbitals per site), together with non-magnetic impurity-potential terms, on a square lattice. The results are trivially generalizable to any bipartite, hypercubical lattice in D dimensions. The Hamiltonian is

$$H = -t \sum_{\langle ij \rangle \sigma} (a_{i\sigma}^{\dagger} a_{\gamma\sigma} + \text{h.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + V \sum_{I} a_{I\sigma}^{\dagger} a_{I\sigma} \tag{1}$$

where $a_{i\sigma}$ and $a_{i\sigma}^{\dagger}$ are the destruction and creation operators for 3d holes of spin σ at site i, V is the (high) impurity potential and the sum Σ_I is over all impurity sites. We consider a filling with one 3d hole for each Cu site remaining in the system, i.e. relative to the half-filled case for the undoped antiferromagnet with one 3d hole per Cu site, one 3d hole is removed for each zinc-type impurity replacing a Cu from the CuO plane. At this filling the system has no mobile holes and is an insulator.

In the undoped case the quantum antiferromagnetic state of the Mott–Hubbard insulator has been studied in detail within a Hartree-Fock-plus-fluctuations approach, and quantum corrections to sublattice magnetization, spin-wave amplitude and the ground-state energy have been evaluated in the strong coupling limit [7]. In fact a systematic procedure for computing quantum corrections has been developed in terms of an inverse-degeneracy expansion scheme which parallels the $1/S$-expansion for spin-S Quantum Heisenberg AF [8]. Thus a good framework exists for studying the effects of doped static impurities in the AF state.

It must be noted here that for the case of doped *mobile* holes in the antiferromagnet (AF), the Hartree-Fock (HF) approach has serious limitations. A self-consistent procedure results in the added hole being self-consistently trapped into a localized spin-bag state, thereby breaking the translational symmetry of the system. The situation is much simpler with static impurities which do in fact break the translational symmetry, and the HF procedure yields a qualitatively correct description of the ground state with AF order, and a good starting point about which quantum fluctuations in conjunction with impurity scattering can be studied.

We have used two different approaches to study the Hubbard model with doped static impurities within the HF approximation. In one scheme we start with the HF description of the undoped AF as the host, and then treat the impurity terms perturbatively within a Green's function formalism. For a single impurity the perturbation can be treated exactly in terms of the T-matrix formalism. This procedure is not fully self-consistent because density modifications introduced by the high impurity-potential terms are not treated self consistently. We therefore supplement this T-matrix analysis with a fully self-consistent numerical study by exact diagonalization of the

HF Hamiltonian on a square lattice with periodic boundary conditions. These results are summarized at the end and presented in more detail elsewhere [9].

We first discuss briefly results of the T-matrix analysis in the AF state. The HF approximation on the Hubbard model yields our unperturbed Hamiltonian,

$$\langle k|H_0^\sigma|k\rangle = \begin{bmatrix} -\sigma\Delta & \varepsilon_{\mathbf{k}} \\ \varepsilon_{\mathbf{k}} & \sigma\Delta \end{bmatrix}$$

in the two-sublattice basis, with quasiparticle energies $E_{\mathbf{k}\sigma\pm} = \pm\sqrt{\Delta^2+\varepsilon_{\mathbf{k}}^2} \equiv \pm E_{\mathbf{k}}$, and quasiparticle amplitudes $(a_{\mathbf{k}\sigma\pm}\, b_{\mathbf{k}\sigma\pm})$ describing the host system [7]. Here 2Δ is the Hubbard gap, $\varepsilon_{\mathbf{k}}$ the free-particle energy on the square lattice, and the quasiparticle amplitudes are given by, $a^2_{\mathbf{k}\sigma\pm} = (1 \mp \sigma\Delta/E_{\mathbf{k}})/2$ and $b^2_{\mathbf{k}\sigma\pm} = (1 \pm \sigma\Delta/E_{\mathbf{k}})/2$. The $\pm$ signs refer to states in the upper and lower Hubbard bands respectively. In terms of quasiparticle amplitudes and energies, the host Green's functions for H_0^σ are given by,

$$g^\sigma(\mathbf{k},\omega) = \left\langle \mathbf{k}\left|\frac{1}{\omega - H_0^\sigma(\mathbf{k})}\right|\mathbf{k}\right\rangle = \sum_s \begin{bmatrix} a^2_{\mathbf{k}\sigma s} & a_{\mathbf{k}\sigma s}b_{\mathbf{k}\sigma s} \\ a_{\mathbf{k}\sigma s}b_{k\sigma s} & b^2_{\mathbf{k}\sigma s} \end{bmatrix} \frac{1}{\omega - E_{\mathbf{k}\sigma s} + is\eta} \quad (2)$$

here s refers to the two signs $+/-$ corresponding to the upper/lower Hubbard band. The Green's function for the single-impurity problem is now given in terms of the T-matrix, $T^\sigma(\omega) = V/(1 - Vg^\sigma_{II}(\omega))$ as

$$G^\sigma_{ij}(\omega) = g^\sigma_{ij}(\omega) + g^\sigma_{iI}(\omega)\, T^\sigma(\omega) g^\sigma_{Ij}(\omega). \quad (3)$$

Information regarding additional poles is contained in the T-matrix, and therefore a study of the local Green's function $g^\sigma_{II}(\omega)$ in the AF state is of the interest. While a detailed analysis of $G^\sigma(\omega)$ will be presented elsewhere [9], the main features are discussed below. If for concreteness we consider the impurity on an A-sublattice site, then using $a^2_{\mathbf{k}\sigma\oplus} = b^2_{\mathbf{k}\sigma\ominus}$ and also $a^2_{\mathbf{k}\sigma\ominus} - b^2_{\mathbf{k}\sigma\ominus} = \sigma\Delta/E_{\mathbf{k}}$, we obtain,

$$g^\sigma_{II}(\omega) = \frac{1}{N}\sum_{\mathbf{k}} \frac{\omega - \sigma\Delta}{\omega^2 - E^2_{\mathbf{k}}}. \quad (4)$$

A plot of $g^\uparrow_{II}(\omega)$ vs ω is given in figure 1 and show logarithmic divergences at energies $\pm\sqrt{\Delta^2+(4t)^2}$, a stronger divergence $(\omega+\Delta)^{-1/2}\ln(\omega+\Delta)$ as $\omega \to -\Delta$ from above, and a $\sqrt{\Delta-\omega}\ln(\Delta-\omega)$ dependence as $\omega \to \Delta$ from below. The intersection with $1/V$ yields the poles, and for large V we obtain a defect state at energy $V - \Delta$ (V relative to the lower band at energy $-\Delta$), and another state inside the Hubbard gap close to the upper band edge. In semiconductor terminology, such gap states arising from defects are referred to as deep traps, and for large V and two similar bands, occur near the mid-gap position. To effect the asymptotic convergence of the trap energy to some fixed position near mid-gap as $V \to \infty$, the concept of pinning has been introduced – large differences in atomic energies influence the trap energies only weakly [10]. The energy separation $\eta \equiv \Delta - E_g$ of the gap state at energy E_g, from the lower edge of the upper Hubbard band is approximately given by $\sqrt{\eta}\ln\eta \sim 1/V$, so that η vanishes essentially as $(1/V)^2$ as $V \to \infty$. For $\downarrow$-spin there is only a defect state and no gap state for positive V. For negative V the gap state appears slightly above the band edge of lower Hubbard band, i.e. slightly above energy $-\Delta$.

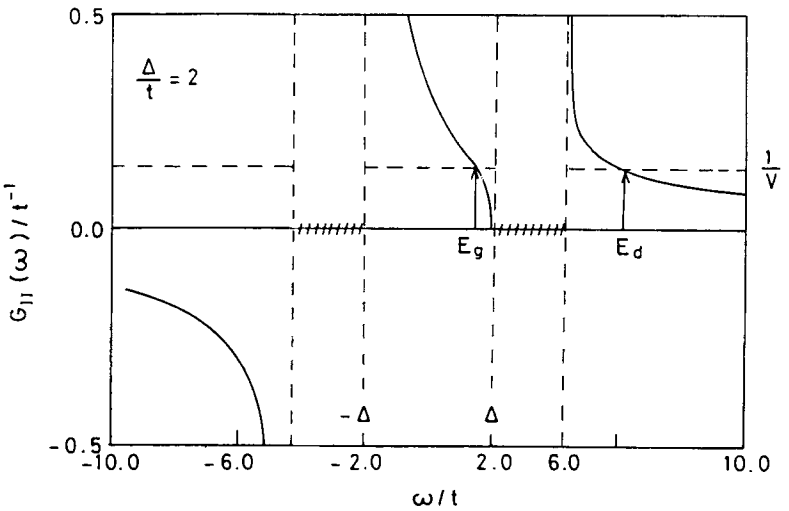

Figure 1. The local host Green's function, $g^{\uparrow}_{II}(\omega)$, in the antiferromagnetic state as a function of ω for regions excluding the two Hubbard bands (shown as hatched). Intersections with 1/V yield gap state (E_g) and the defect state (E_d).

Both the defect state and the gap state, lying as they do outside the AF band, are localized. The defect state is essentially site localized on the impurity sites in the strong coupling limit. The gap-state has amplitude mainly on the B-sublattice site in the strong coupling limit and for large V. In the $V \to \infty$ limit, the gap-state wavefunction goes as $\Sigma_{\mathbf{k}} \varepsilon_{\mathbf{k}}^{-1} e^{i\mathbf{k}.\mathbf{r}}$, which exhibits a power-law fall-off at large distances. From (3) the change in the Green's function, $\delta G_{ij}(\omega) = G_{ij}(\omega) - g_{ij}(\omega)$, due to impurity scattering can be written, for energies outside the band and very close to the gap-state energy, E_g, as:

$$\delta G_{ij}(\omega \sim E_g) = \frac{g_{iI}(E_g)\left[-\left.\frac{\partial g_{II}(\omega)}{\partial \omega}\right|_{\omega = E_g}\right]^{-1} g_{Ij}(E_g)}{\omega - E_g + i\eta} \tag{5}$$

where $g_{II}(\omega)$ has been Taylor-expanded near E_g, and we have used $1 - V g_{II}(E_g) = 0$ which determines E_g. The above equation can be rewritten in the following form, yielding the gap-state Green's function in terms of $\phi^i_g \equiv g_{iI}(E_g)/\sqrt{-\partial g_{II}(\omega)/\partial\omega|_{E_g}}$, which gives the amplitudes for the gap state,

$$\delta G_{ij}(\omega \sim E_g) = \frac{\phi^i_g \phi^j_g}{\omega - E_g + i\eta}. \tag{6}$$

We now examine the nature of the gap-state wavefunction, $\phi_g(\mathbf{r})$ where $\mathbf{r} \equiv \mathbf{r}_i - \mathbf{r}_I$ is the relative positive vector. $\phi^{\uparrow}_g(\mathbf{r})$ is proportional to $g^{\uparrow}(\mathbf{r}, \omega = E_g)$ and, for site i belonging to the A-sublattice, is therefore given by,

$$\phi^{\uparrow}_g(\mathbf{r}) \sim \frac{1}{N} \sum_{\mathbf{k}} \frac{E_g - \Delta}{E_g^2 - E_{\mathbf{k}}^2} e^{i\mathbf{k}.\mathbf{r}} \tag{7}$$

In the large V limit, as $V \to \infty$, the gap-state wavefunction therefore has vanishingly small amplitudes on A-sublattice sites as $E_g \to \Delta$ in this limit. A similar analysis, with use of the identity $a_{\mathbf{k}\uparrow\ominus} b_{\mathbf{k}\uparrow\oplus} = \varepsilon_{\mathbf{k}}/2E_{\mathbf{k}}$, shows that on B-sublattice sites the gap-state wavefunction is given by,

$$\phi_g^{\uparrow}(\mathbf{r}) \sim \frac{1}{N} \sum_{\mathbf{k}} \frac{\varepsilon_{\mathbf{k}}}{E_g^2 - E_{\mathbf{k}}^2} e^{i\mathbf{k}.\mathbf{r}} \tag{8}$$

Again, in the large V limit, as $E_g \to \Delta$, the gap-state wavefunction is given by $\phi_g(\mathbf{r}) \sim \Sigma_{\mathbf{k}} \varepsilon_k^{-1} \exp(i\mathbf{k}.\mathbf{r})$. At large x and y distances, the long-wavelength modes contribute predominantly, and this yields a power-law fall-off, $\phi_g(\mathbf{r}) \sim 1/xy$.

We believe that these gap states which are occupied with electrons and localized around the impurity sites are responsible for the presence of local moments observed in these systems. For a zinc atom sitting on an A-sublattice site, the gap state is occupied by an $\uparrow$-spin electron. In terms of electrons, the dopant site is occupied by two electrons (empty of holes), and there are $(N-1)$ $\uparrow$-spin and $\downarrow$-spin electrons in the antiferromagnetic band states (in the upper Hubbard band). These electrons form compensated spin systems, and therefore should contribute an essentially temperature-independent (for $T \ll J$) magnetic susceptibility. The lone electron in the localized gap state behaves essentially like a free spin in the dynamical state when there is no barrier between the up and down spin states, and hence should have a Curie-type $1/T$ contribution.

Such a magnetic behaviour has been well established in zinc-doped cuprates in cases where local AF order is present [1,2], as has been the observation that the local moments responsible for the paramagnetic behaviour are present predominantly on Cu sites neighbouring the dopant site [4].

All these results regarding the defect and gap states obtained via the T-matrix approach as described above have been verified using a fully self-consistent numerical study of the AF system on a finite lattice. It becomes clear that the response of the host (AF) system to the insertion of the impurity is a higher-order correction. In this unrestricted Hartree-Fock approach the HF Hamiltonian with the impurity-potential term is diagonalized exactly on a finite lattice with periodic boundary conditions, and local spin densities evaluated to update the HF Hamiltonian, and the procedure is iterated till self-consistency is obtained. In this study density modifications caused by the high impurity potential are allowed and treated self-consistently. Detailed results of this study are presented elsewhere [9].

We now qualitatively discuss effects of additional doping with holes in the static-impurity-doped antiferromagnet. Each gap state produced by the static impurity can trap one added hole into the localized state, and an added hole going in the gap state will, at the HF level, remove the local-moment associated with the gap state. However, fluctuations – both thermal as well as quantum – will result in some spectral weight of electrons in the gap states, and hence the local moments will persist even with additional holes. With further addition of holes the situation is not very clear as the exact nature of the ground state of the Hubbard model away from half-filling is itself not unambiguously known at present. Long-range AF order is believed to be destroyed efficiently by hole doping, and the qualitative picture that is emerging is that the added holes from states with vanishingly small Fermi-liquid-type coherent weight and a predominantly incoherent spectral function. This qualitative picture is

presented solely to suggest that the mobile holes in a doped Mott–Hubbard system do see the presence of local moments produced by gap states.

The situation is relatively simpler within the three-band picture of cuprates, with a predominantly oxygen-like band lying between the two predominantly copper-like Hubbard bands. The gap states in this case are still expected to be close to the upper Hubbard band. Added holes go in the oxygen-like band which is well below the upper Hubbard band, and therefore, the local moment formation due to the gap states is robust with respect to additional hole doping in this case – even at HF level.

Coming now to the dynamics of the local moments formed by the occupied gap states, it is clear that when long-range AF order exists, which is frozen in time the local-moment direction is also fixed, and the system should hence resemble a spin glass with frozen moments. With long-range AF order destroyed by the mobile holes, the local-moment direction fluctuates in time following the local staggered-magnetization direction, and therefore the local moment behaves, over times scales long compared to the dynamical time scale of the fluctuating local order, as a free spin. Therefore in the dynamical, spin-disordered state with fluctuating local order, the local moment associated with the gap state should yield a Curie-type susceptibility.

In conclusion, static, non-magnetic impurities have been shown to give rise to gap states in addition to defect states in a Mott–Hubbard antiferromagnet. The gap states are pinned at the band edges. The gap-state wavefunction falls-off as a power-law away from the dopant site. Electrons occupying gap states are argued to be responsible for the local-moment behaviour observed in systems such as zinc-doped cuprate antiferromagnets. The local-moment distribution is predominantly on sites neighbouring the dopant zinc sites, as has been seen in recent Y-NMR studies [4]. The local-moment associated with the gap states should also be present within the three-band Hubbard model of copper-oxides, even after doping with mobile holes. It should therefore be of interest to examine the scattering of carriers and of superconducting pairs off these local moments, and to see whether any enhancement in pair-breaking results from their extended size. Recent quantitative attempts to correlate the reduction in the superconducting transition temperature with impurity concentration within standard Abrikosov's pair-breaking theory have ranged from complete disagreement [6] to order-of-magnitude agreement [4]. An RPA-level study of spin-wave spectral properties is currently under progress. Self-energy corrections to the spin-wave propagator due to impurity scattering should be of interest for studying the magnetic dynamics in doped antiferromagnets due to thermal excitation. Such an analysis, with interlayer coupling and anisotropy effects appropriately included, will be useful for a quantitative understanding of the Néel-temperature variation of cuprate antiferromagnets with (zinc) doping concentration [11, 12].

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References

[1] C S Gee *et al*, *J. Superconductivity* **1**, 63 (1988)
[2] G Xiao, M Z Cieplak and C L Chien, *Phys. Rev.* **B42**, 240 (1990a)
[3] H Alloul, P Mendels, H Casalta, J F Marucco and J Arabski, *Phys. Rev. Lett.* **67**, 3140 (1991)

[4] A V Mahajan, H Alloul, G Collin and J F Marucco, *Phys. Rev. Lett.* **72**, 3100 (1994)
[5] G Xiao, M Z Cieplak, J Q Xiao and C L Chien, *Phys. Rev.* **B42**, 8752 (1990b)
[6] R E Walstedt, R F Bell, L F Schneemeyer, J V Waszczak, W W Warren Jr, R Dupree and A Gencten, *Phys. Rev.* **B48**, 10646 (1993)
[7] A Singh and Z Tešanovic, *Phys. Rev.* **B41**, 11457
[8] A Singh, *Phys. Rev.* **B43**, 3617 (1991)
[9] S Basu and A Singh, 1994 (to be published)
[10] H P Hjalmarsson, P Vogl, D J Wolford, J D Dow, *Phys. Rev. Lett.* **44**, 810 (1980)
[11] S W Cheong, A S Cooper, L W Rupp, B Batlogg, J D Thompson and Z Fisk, *Phys. Rev.* **B44**, 9739 (1991)
[12] B Keimer, A Aharony, A Auerbach, R J Birgeneau, A Cassanho, Y Endoh, R W Erwin, M A Kastner and G Shirane, *Phys. Rev.* **B45**, 7430 (1992)