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On the stability of hole crystals in layered cuprates

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Abstract. Recent STM measurements have revealed the existence of periodic charge modulations at the surface of certain cuprate superconductors. Here we show that the observed patterns are compatible with the formation of a three-dimensional crystal of doped holes, with space correlations extending between different Cu-O layers. This puts severe constraints on the dynamical stability of the crystallised hole structure, resulting in a close relationship between the periodicity of the electronic modulation and the interlayer distance.

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Since the discovery of high temperature superconductivity, several microscopic models have been proposed in order to explain the complex phase diagram of the cuprates. In particular, the presence of an antiferromagnetic phase in the parent compounds has led to a huge theoretical effort on models with local electronic interactions, such as the Hubbard or t-J models. It is seldom realised that, when few carriers are added to an insulating system by doping, the long range part of the Coulomb repulsion is not screened, and can not be neglected *a priori*.

Interest in the long range interactions has been recently revived by the observation, by scanning tunneling microscopy, of periodic modulations of the electronic density of states at the surface of the cuprate compounds $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) [1–8] and $Ca_{2-x}Na_xCuO_2Cl_2$ (Na-CCOC) [9]. Although some of the features have been interpreted in terms of quasi-particle interference effects, the emergence of modulations with a dispersionless ordering vector $q \simeq 2\pi/4a_0$ directed along the Cu-O bonds, strongly points to the existence of an underlying charge order, characteristic of the less conducting (pseudogap) regions. Among other possibilities, the latter could be ascribed to the formation of a Wigner crystal [10] of holes [9, 11–15] — an insulating ordered state arising in electronic systems at low density, when the long-range Coulomb interactions are dominant — or to the ordering of hole pairs [16–19].

The aim of this work is to determine if the concept of hole crystallisation is compatible with the experimental observations in the cuprates. It is clear that a complete microscopic treatment of the problem should consider, in addition to the aforementioned long range Coulomb repulsion, also the interaction of the doped holes with all the degrees of freedom of the host material, including the $1-x$ localised electrons in the Mott insulator, the ions of the host lattice, chemical impurities, etc... Instead of attempting this formidable task, or choosing to rely on a definite microscopic model, we shall approach the problem starting from the experimental observation that the holes *are* localised in an ordered pattern, and describe the system in the framework of a phenomenological Lorentz model. As we will show, a great insight into the problem can be gained already at this phenomenological level, leading to precise constraints on the admissible shape and periodicity of the charge ordering patterns.

Let us consider the holes to be located at the sites $\mathbf{R_i}$ of a *three-dimensional* Bravais lattice. This is a sensible assumption because, despite the structural constraints in the cuprates, which confine the carrier motion into Cu-O layers, the long range Coulomb interactions are isotropic, so that the ordering within a Cu-O layer is certainly affected by the positions of the holes on different layers. Allowing for small (inplane) displacements $\mathbf{R_i} \to \mathbf{R_i} + \mathbf{u_i}$ around the equilibrium positions leads to the following quadratic Hamiltonian:

$$H_I = \sum_i H_i + \frac{1}{2\epsilon_\infty} \sum_{i \neq j} u_i^\alpha \mathcal{I}_{ij}^{\alpha\beta} u_j^\beta + \sum_i \frac{1}{2} m\omega_0^2 u_i^2. \quad (1)$$

The first term on the right represents all the *static* long-range Coulomb interaction effects, including the Madelung

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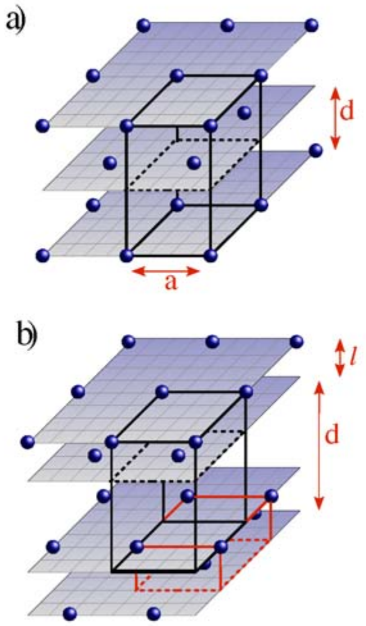

Fig. 1. The anisotropic crystal structures considered in the text: a) single layer compounds (d is the interlayer spacing, a is the hole-hole distance within a layer); b) bilayer compounds (l is the distance between neighbouring layers).

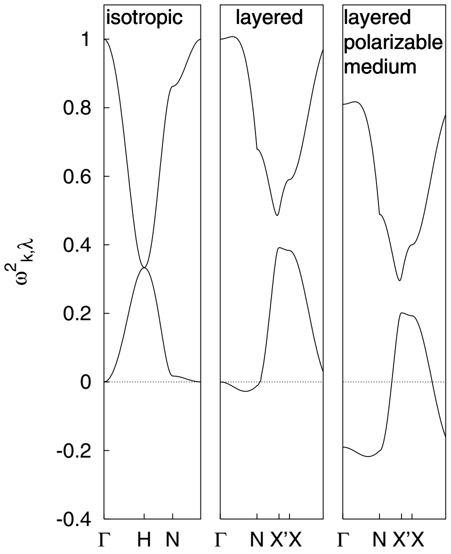

Fig. 2. Spectrum of the collective excitations of different Wigner crystals, for wavevectors k within the plane. Left panel: the usual body centered cubic (BCC) Wigner lattice ($\gamma = 1$). Center panel: anisotropic BCT lattice with $\gamma = 0.5$, which is unstable against shear, as signaled by the existence of purely imaginary solutions with $\omega^2_{\mathbf{k}\lambda} < 0$. Right panel: the same anisotropic lattice embedded in a polarisable medium with $\eta = \epsilon_\infty/\epsilon_s = 0.5$. The eigenvalues are expressed in units of $\omega_p^2 = 4\pi n e^2/m\epsilon_\infty$, m being the hole mass, and n the hole density. The symmetry points indicated in the graphs are defined as follows, in units of π/a. Left panel: $\Gamma = (0,0)$, H$= (2,0)$, N$= (1,1)$. Centre and right panel: $\Gamma = (0,0)$, N$= (1+\gamma^2, 0)$ X$' = (1+\gamma^2, 1-\gamma^2)$, X$= (1,1)$.

energy of the Bravais lattice, plus the restoring potentials acting at each $\mathbf{R_i}$, due to the repulsion of the other holes localised at $\mathbf{R_j} \neq \mathbf{R_i}$. The second term is the usual dipole-dipole interaction arising between particle oscillations. The indices $\alpha, \beta = x, y$ are summed, and $\mathcal{I}^{\alpha\beta}_{ij} = \frac{|R_{ij}|^2\delta^{\alpha\beta} - 3R^{\alpha}_{ij}R^{\beta}_{ij}}{|R_{ij}|^5}$. It should be noted that the terms H_i are screened by the static dielectric constant ϵ_s of the host medium, while the dipolar interactions between fast hole oscillations are ruled by the high frequency dielectric constant ϵ_∞. This discrepancy can have important consequences in the cuprates, where ϵ_s is substantially larger than ϵ_∞ owing to the ionic polarisability. The last term represents the (unknown) potential which, within our phenomenological approach, accounts for the influence of the host material on the dynamics of the individual holes (interaction with the magnetic, ionic degrees of freedom...).

Let us first consider a “pure” Wigner crystal, which is obtained by setting $\omega_0 = 0$ in the above Hamiltonian [20]. Among the different three-dimensional Bravais lattices compatible with the structural anisotropy imposed by the Cu-O layers, we shall deliberately restrict ourselves to the cases which present a *square* charge ordering within the planes, as observed in experiments. Within this subclass, it can be demonstrated that the body centered tetragonal (BCT), illustrated in Figure 1a., has the lowest Madelung energy.

To determine if such anisotropic Wigner crystal is stable, we now evaluate the frequencies $\omega_{\mathbf{k}\lambda}$ (λ = branch index) of the corresponding collective charge density oscillations. The calculation is performed using standard Ewald summation techniques, at different values of the anisotropy ratio $\gamma = a/2d$ (a being the inplane interparticle spacing, determined by the hole concentration, and d the interlayer distance). The excitation spectra are reported in Figure 2. In the isotropic case ($\gamma = 1$, left panel), we recover the body centered cubic (BCC) structure, which is known to be mechanically stable. Generic BCT crystals are also stable for weak anisotropy ratios within the range $0.66 < \gamma < 1.07$. Note that this identifies an interval of hole concentrations, where a square ordering in the planes arises naturally due to the three-dimensional character of the Coulomb interactions.

For anisotropy ratios outside the range $0.66 < \gamma < 1.07$, the emergence of imaginary eigenfrequencies ($\omega^2_{\mathbf{k}\lambda} < 0$, see Fig. 2, central panel) signals that the BCT structure considered here is, in principle, mechanically unstable, so that the preferred Wigner crystal structure has a different symmetry. However, energetic differences between competing structures are expected to be very small, since Madelung energies are essentially determined by long range effects. Therefore, it is likely that the observed hole distributions are influenced by other microscopic mechanisms, such as the commensurability with the Cu-O host lattice, which justifies our restriction to square planar orderings [21].

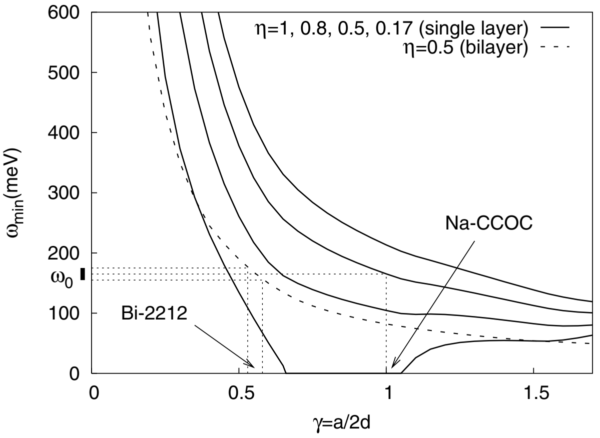

Fig. 3. The characteristic energy scale of the trapping potential necessary to stabilise an anisotropic hole crystal, as a function of the anisotropy ratio γ. Full lines correspond to the single layer host structure of Na-CCOC, with $d = 7.75$ Å and $\epsilon_\infty = 4.5$, at different values of the polarisability ratio (from left to right, $\eta = 1, 0.8, 0.5, 0.17$). The dashed line is for the bilayer structure of Bi-2212, with $\epsilon_\infty = 4.9$ and $\eta = 0.5$. The system becomes increasingly unstable upon increasing the hole concentration (i.e. reducing γ). The different periodicities observed in Na-CCOC and in Bi-2212 (indicated by arrows) correspond to a common localisation energy ~ 0.16 eV, characteristic of the host cuprate materials.

Let us now consider a crystal of holes embedded in a polarisable medium. In this case, an additional source of instability appears, causing an overall downward shift of the excitation spectrum (Fig. 2, right panel). This occurs because, owing to the *ionic polarisability* (i.e. as soon as $\eta = \epsilon_\infty/\epsilon_s < 1$), the static restoring potentials that localise the holes, and their mutual dipolar interactions, responsible for the dispersion of the collective frequencies, are screened by different dielectric constants. We conclude that some additional localising mechanism is required to stabilise a hole crystal in polarisable media such as the cuprates, and turn our attention to the full Lorentz model of eq. (1). The collective frequencies $\Omega_{\mathbf{k}\lambda}$ in this case can be derived straightforwardly from the solution of the pure Coulomb problem as [20]:

$$\Omega^2_{\mathbf{k}\lambda} = \omega^2_{\mathbf{k}\lambda} + \omega^2_0. \tag{2}$$

Mechanical stability requires that the eigenfrequencies $\Omega_{\mathbf{k}\lambda}$ are all real. This, according to equation (2), sets a lower bound on the energy scale of the localising potential: $\omega_0^2 \geq \omega^2_{min}$, where ω^2_{min} is defined as the modulus of the most negative eigenvalue $\omega^2_{\mathbf{k}\lambda}$ over the Brillouin zone. This quantity is reported in Figure 3 as a function of γ, for different values of the polarisability ratio η. We see that it is low and flat at large γ (i.e. at low hole concentrations), but it rises sharply for $\gamma \approx< 0.5$, indicating that charge patterns whose inplane periodicity is much shorter than the interlayer distance are very unlikely to occur, since these can only be stabilised by invoking an additional localisation mechanism with a very large energy scale. This general observation establishes a direct link between the admissible periodicity of the charge modulations —an electronic property— and the distance between Cu-O layers —a structural constraint. To be more specific, using the appropriate values $d = 7.75$ Å, $a_0 = 3.85$ Å, $\epsilon_\infty = 4.5$ and $\eta \approx 0.5$ [22] for Na-CCOC, it can be read directly from Figure 2 that the observed periodicity $a = 4a_0$ ($\gamma = 1$) *implies* that the characteristic energy scale involved in the localisation of the holes is (at least) $\omega_0 \approx 0.16$ eV.

If the proposed picture is correct, it should apply to other cuprates, such as the bismuth based $Bi_2Sr_2CaCu_2O_{8+\delta}$. These compounds present an additional constraint related to the bilayer structure, for which the corresponding lowest energy configuration is illustrated in Figure 1b. As in the single layer case, the calculated excitation spectrum shows that a pure Wigner crystal of holes is unstable due to the ionic polarisability, and an additional source of localisation must be considered. Repeating the same arguments as in Na-CCOC, with parameters $d = 15.5$ Å, $l = 3$ Å and dielectric constants $\epsilon_\infty = 4.9$, $\eta \approx 0.5$ [23], we read from Figure 3 (dashed line) that the observed periodicities $a/a_0 = 4.3 - 4.7$ [1,4,6–8] ($\gamma = 0.53 - 0.58$) are stabilised by taking $\omega_0 = 0.15$–0.17 eV, which is remarkably close to the value obtained in Na-CCOC. This result strongly points to the existence of a *common* localisation mechanism, which could be at the origin of the different periodicities observed in different compounds. Following the same steps in the case of the single layer compound $Bi_2Sr_2CuO_6$, which has a shorter interlayer distance than Na-CCOC ($d = 12.3$ Å), we predict a crystal periodicity $a/a_0 \approx 3.4$ that would be interesting to verify experimentally.

Before enquiring about its microscopic foundations, let us analyse the consequences of the present scenario. First of all, since ω_0 reflects the interaction of individual holes with the host material, in principle it should not depend much on the doping level. Here we take it as a constant, characteristic of the parent cuprate compounds. According to equation (2), in the limit of vanishing hole density, where all the $\omega_{\mathbf{k}\lambda} \to 0$, the excitation spectrum will be dominated by ω_0. Upon increasing the hole concentration, however, the collective frequencies spread away from ω_0 due to the term $\omega^2_{\mathbf{k}\lambda}$, which admits both positive and negative values. As a consequence, the longitudinal charge oscillations get hardened upon doping, while transverse oscillations are progressively softened, until a given eigenfrequency $\Omega_{\mathbf{k}=\mathbf{k}_c}$ vanishes, leading to a *polarisation catastrophe* at a critical concentration x_c [13,20,24,25]. The predicted softening of long wavelength transverse oscillations, [13,25] which is entirely due to the long-range polarisability of the medium, has been experimentally observed in systematic studies of the optical conductivity spectra of both electron- and hole-doped cuprates in the underdoped region [26,27]. Similar signatures of the polarisation catastrophe can be expected in spectroscopic ellipsometry and electron energy loss spectroscopy.

In the foregoing discussion, we have assumed that all of the doped holes are crystallised, so that the system is insulating for $x < x_c$. In this case, the periodicity of the modulation varies continuously with x until it reaches its limiting value $a/a_0 = (n_l/x_c)^{1/2}$ at the critical concentration ($n_l = 1, 2$ for single and bilayer host structures) [28]. When further holes are doped into the system beyond x_c, these can not be accommodated in the crystallised state, which is at the border of an instability. If, as indicated by experiments, the hole crystal survives for $x > x_c$, one possibility is that the excess holes settle in the interstitials of the main ordering pattern, creating a superimposed modulation, as observed in the Na-CCOC samples [9]. Another possibility is that the system phase separates into insulating (crystallised) and conducting regions, as seems to be the case in Bi-2212 [7]. The question of crystal stability in the presence of additional mobile charges, and the consequent screening of the long range interactions, remains open.

Based on the emerging scenario, we can now speculate on the microscopic mechanism underlying the localisation of the holes. First of all, the energy scale ω_0 identified above is definitely too large to be imputed exclusively to the binding potentials of chemical impurities, or to the pinning by commensurability effects [29]. On the other hand, the interaction with the antiferromagnetic background, which is ruled by typical exchange energies $J \sim 0.1$ eV, would constitute a viable possibility. However, in strongly polarisable materials, the excess charges added by doping are expected to form dielectric polarons. Indeed, it can be recognised that the value of ω_0 derived in this work coincides with the locus of a well defined absorption band, ubiquitous in the infrared optical spectra $\sigma(\omega)$ of strongly underdoped cuprates, which is generally ascribed to the formation of polarons [30], suggesting that the additional mechanism required to stabilise the hole crystal is the *polaron self-trapping potential* [31]. The Wigner crystallization of polarons in the insulating phase of the cuprates has been proposed independently by Remova et al. [11], and Quémerais [12]. The quantum melting of such polaron crystal has been studied in references [13, 25, 32, 33] yielding similar conclusions as in the present paper.

Our analysis demonstrates that the periodic modulations observed at the surface of the cuprates are compatible with the crystallisation of holes, arising due to the combined effects of the long range Coulomb interactions, and of some additional localising phenomenon, whose characteristic energy scale is $\omega_0 \sim 0.16$ eV. Although several microscopic mechanisms can be involved, polaron formation appears as a good candidate to stabilise a hole crystal in the cuprates.

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28. Assuming for simplicity that the Lorentz local field factor of the crystallised structure at the concentrations of interest does not deviate significantly from the isotropic case, we can write the following approximate expression for the critical concentration:

    $$x_c = \frac{3\epsilon_\infty}{16\pi(1-\eta)}\left(\frac{\hbar\omega_0}{Ryd}\right)^2 \frac{d a_0^2}{a_B^3}$$

    where a_B is the Bohr radius and $Ryd = 13.6$ eV. Taking $\epsilon_\infty \approx 4.5$, $\eta \approx 0.5$ and $\omega_0 \approx 0.16$ eV yields $x_c = 3.9 \times 10^{-3}(d/a_B)$ which gives $x_c \approx 0.05$–0.11 for several cuprate crystal structures, with corresponding modulations $a/a_0 \approx 3.5$–6
29. Although they certainly favor charge ordering, commensurability effects decrease drastically when moving away from simple fractional fillings, and it has been shown that they do not dominate the Wigner crystal stability at low concentrations [see e.g. Y. Noda, M. Imada, Phys. Rev. Lett. **89**, 176803 (2002); H. Falakshahi et al., Eur. Phys. J. B **39**, 93 (2004)]
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