Dynamical charge inhomogeneity and crystal-field fluctuations for 4f ions in high-T_c cuprates

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The main relaxation mechanism of crystal-field excitations in rare-earth ions in cuprates is believed to be provided by the fluctuations of crystalline electric field induced by a dynamic charge inhomogeneity generic for the doped cuprates. We address the generalized granular model as one of the model scenario for such an ingomogeneity where the cuprate charge subsystem remind that of Wigner crystal with the melting transition and phonon-like positional excitation modes. Formal description of R-ion relaxation coincides with that of recently suggested magnetoelastic mechanism.

Inelastic neutron scattering (INS) spectroscopy is a powerful tool to determine unambiguously the Stark multiplet structure and crystal-field (CF) potential in rare-earth (R) based high-T_c superconducting materials such as $Y_{1-x}R_xBa_2Cu_3O_{6+y}$.[1,2] This technique provides detailed information on the electronic ground state of the R-ions which is important to understand the thermodynamic magnetic properties as well as the observed coexistence between superconductivity and long-range magnetic ordering of the R-ion sublattice at low temperatures. Moreover, INS spectroscopy is addressed to be a powerful tool for a quantitative monitoring the decay of the antiferromagnetic state of the parent compound as well as the evolution of the superconducting state upon doping, since the linewidths of CF transitions are believed to directly probe the electronic susceptibility. The relaxation behavior appears to be extremely dependent upon the energy at which the susceptibility is being probed. The crystal-field INS spectroscopy is widely used to reveal the opening of an electronic gap in the normal state of underdoped superconductors[1] and examine its anisotropy.[3,4] Recently, the Ho^{3+} CF-INS spectroscopy was used to investigate the oxygen and copper isotope effects on the pseudogap in the high-temperature superconductors Ho-124 and $(LaHoSr)_2CuO_4$.[5,6] However, the mechanism of the relaxation of rare-earth ions in cuprates becomes the issue of hot debates,[7,8] that questions the current interpretation of information detected by INS spectroscopy.

In the normal state the excited crystal-field levels of R-ion interact with phonons, spin fluctuations, and charge carriers. These interactions limit the life-time of the excitation; thus the observed crystal-field transitions exhibit line broadening. Similarly the conventional Fermi-liquid metals the interaction with the charge carriers is by far considered to be the dominating relaxation mechanism in cuprates. This interaction is usually assumed to be isotropic exchange coupling with effective spin-Hamiltonian $H_{ex} = -2I(g_J - 1)(\mathbf{s} \cdot \mathbf{J})$, where I is exchange integral that should be nearly independent of the particular R-ion under consideration, g_J Lande factor, $\mathbf{s}$ is the spin momentum of a charge carrier, and $\mathbf{J}$ the total momentum of R-ion. Such a scenario seems to be a rather natural, if taking into account the predominant spin channel of neutron scattering. The detailed theory of the respective relaxation mechanism was developed by Becker, Fulde and Keller (BFK-model).[9] The corresponding intrinsic linewidth appears to increase almost linearly with temperature ($\Gamma(T) \propto \rho^2 T$) according to the well-known Korringa law.[10] Here ρ is the *coupling constant*: $\rho = I(g_J - 1)N(E_F)$, where $N(E_F)$ is the density of states (DOS) at the Fermi level. Namely the deviation from a linear temperature dependence at low temperatures has been usually interpreted in terms of the opening of a (pseudo)gap and the associated reduction in the damping. Fitting the high-temperature linewidth data in frames of simple or modified Korringa law one obtains the values of *coupling constant* which typically vary from 0.003 to 0.006.[1,3,4,5,6]

It should be emphasized that the spin channel of relaxation implies directly the relevance of the Fermi liquid scenario for cuprates ignoring many signatures of non-Fermi liquid behavior. However, it is unlikely to be a shortcoming of either model approach whether it were intrinsically self-consistent. However, the spin-exchange model has a number of visible inconsistencies, firstly as concerns the magnitude of *coupling constant*. Indeed, a linear temperature dependence of the relaxation time above T_c observed in EPR studies of S-ion Gd^{3+} in $YBa_2Cu_3O_7$ after Korringa fitting yields the magnitude of exchange integral $I \approx 3 \times 10^{-4}$ eV (Ref.12) that directly points to an unrealistically big values of spin coupling constants ρ found in all the INS experiments on CF transitions. Some problems exist with a Lande factor $\propto (g_J - 1)$ scaling. So, Mukherjee *et al.*[11] when studying the system $Y_{1-x}R_xBa_2Cu_3O_{6+y}$ (R=Er, Ho, Tm) found $|\frac{\rho(Tm)}{\rho(Ho)}| \simeq 2$, instead of theoretically expected $\frac{(g_{Tm}-1)}{(g_{Ho}-1)} = \frac{2}{3}$, and $|\frac{\rho(Tm)}{\rho(Er)}| \simeq 4.5$, instead of expected $\frac{(g_{Tm}-1)}{(g_{Er}-1)} = \frac{5}{6}$. This clear disagreement evidences against exchange mechanism. The spin-exchange scenario fails to explain the "strange" doping dependence of Tm^{3+} relaxation in Tm-123[13] and Nd^{3+} relaxation in $(LaSrNd)_2CuO_4$.[14]

Finally, Staub *et. al.*[15] have found that the Lorentzian linewidth of the quasi-elastic neutron scattering for Tb^{3+} in $YBa_2Cu_3O_7$ can be properly described by a simple $(exp(\Delta/k_BT) - 1)^{-1}$ law typical for Orbach processes

governed by lattice vibrations. They have shown that such an interpretation also describes the results obtained earlier on Ho^{3+} and Tm^{3+}. They conclude that the interactions with the charge carriers are negligible and that the interactions with the lattice vibrations are responsible for the relaxation behaviour of the 4f electrons in cuprates. Therefore, the INS results which claim to probe the superconducting gap or the pseudo-gap should be re-examined in terms of Orbach processes. Similar conclusion was drawn by Roepke *et. al.*[14] for Nd^{3+} relaxation in $(LaSrNd)_2CuO_4$. Lovesey and Staub[16] have shown that the dynamic properties of the lanthanide ions (Tb^{3+}, Ho^{3+}, and Tm^{3+} are adequately described by a simple three-state model not unlike the one introduced by Orbach for the interpretation of electron paramagnetic resonance signals from a lanthanide ion in dilute concentration in a salt. The cross section for inelastic scattering of neutrons by the lanthanide ion is derived by constructing a pseudospin S=1 model and treating the magnetoelastic interaction as a perturbation on the three crystal-field states. The scattering of neutrons is thus a quasielastic process and the relaxation rate is proportional to $(exp(\Delta/k_BT)-1)^{-1}$, where Δ is the energy of the intermediate crystal-field state at which the density of phonon states probed. However, this very attractive scenario also faces some visible difficulties with the explanation, for instance, of the unusual nonmonotonic temperature dependences and too large oxygen isotope effect in the INS spectra of Ho-124 and Ho-214 systems,[5,6] some doping dependences in Nd-214 system.[14]

On comparing two mechanisms we should underline their difference which seems to be of primary importance: the spin-channel mechanism takes into account the fluctuations of *effective magnetic field* on R-ion, while the phonon (magnetoelastic) mechanism deals with that of *electric field*. Moreover, the conventional spin-channel mechanism actually probes *spin fluctuations* rather than *charge fluctuations*, albeit its contribution to the linewidth $\Gamma(T) \propto (I\,N(E_F)^2$ is believed to strongly depend on the density of carriers. However, this relationship is derived in frames of Fermi liquid scenario, and would be modified, if one addresses the typical antiferromagnetic insulating state. Interestingly, that in Refs.8,15,16 the phonon (magnetoelastic) mechanism is addressed as an alternative to the charge fluctuations. As an example, the authors point to insulating materials where "...the density of carriers is essentially zero...",[8] that forbids the charge fluctuation channel of relaxation.

We would like to emphasize the fact that both groups of researchers underestimate the role of the R-ion relaxation due to a conventional *spinless charge fluctuation channel*. Indeed, the CF Hamiltonian for R-ion in cuprate can be written in its standard form as follows:

$$H_{CF} = \sum_{k=2,4,6} \sum_{-k\le q\le k} B^*_{kq}\hat{O}^q_k.$$

Here $\hat{O}^q_k$ are Stevens equivalent operators, $B_{kq} = b_{kq}\langle r^k\rangle\gamma_k$, where b_{kq} are CF parameters, $\gamma_2 = \alpha$,$\gamma_4 = \beta$, $\gamma_6 = \gamma$ (α, β, γ are Stevens parameters);

$$b_{kq} = \langle b_{kq}\rangle + \Delta b_{kq},$$

which may be expressed in frames of the well-known point-charge model as follows:

$$\Delta b_{kq} = \sum_i \frac{qC^k_q(\mathbf{R}_i)}{R^{k+1}_i}(\hat{n}_i(t) - \langle n_i\rangle),$$

where C^k_q is the spherical harmonics, $\hat{n}_i(t)$ the charge number operator. Conventional metals are characterized by a very short-time charge dynamics that allows to neglect the contribution of charge fluctuations to the relaxation of R-ions in the low-energy range of CF energies, and deal with a mean homogeneous charge distribution. An altogether different picture emerges in the case of cuprates where we deal with various manifestations of static and dynamic charge inhomogeneity(see, e.g. Refs.17,18 and references herein). Moreover, the INS spectroscopy of CF excitations itself yields the impressive picture of charge inhomogeneity in 123 system,[1,2] where it was found that the observed CF spectra separate into different local components whose spectral weights distinctly depend on the doping level, i.e., there is clear experimental evidence for cluster formation. The onset of superconductivity can be shown to result from percolation which means that the superconductivity is an inhomogeneous materials property. It seems probable that the dynamical rearrangement of the charge system at the temperatures above T_c somehow affects the R-ion relaxation.

At present the stripe model of inhomogeneity[18] became the most popular. This model is based on the more universal idea of topological phase separation, when the doped particles are assumed to localize inside the domain walls of a bare phase.

Below we address one of the topological phase separation scenario which may be termed as *a generalized granular model for doped cuprates*. We assume that the CuO_2 layers in parent cuprates may gradually loose its stability under electron/hole doping, while a novel self-organized multigranular 2D phase is believed to become stable. Such a situation resembles in part that of granular superconductivity.

The most probable possibility is that every micrograin accumulates one or two particles. Then, the number of such entities in a multigranular texture nucleated with doping has to nearly linearly depend on the doping. Generally speaking, each individual micrograin may be characterized by its position, nanoscale size, and the orientation of U(1) degree of freedom. In contrast with the uniform states the phase of the superfluid order parameter for micrograin is assumed to be unordered. The granular structure must be considered as being largely dynamic in nature.

In the long-wavelength limit the off-diagonal ordering can be described by an effective Hamiltonian in terms of U(1) (phase) degree of freedom associated with each

micrograin. Such a Hamiltonian contains a repulsive, long-range Coulomb part and a short-range contribution related to the phase degree of freedom. The latter term can be written out in the standard for the XY model form of a so-called Josephson coupling

$$H_J = -\sum_{\langle i,j\rangle} J_{ij}\cos(\varphi_i - \varphi_j), \qquad (1)$$

where φ_i, φ_j are global phases for micrograins centered at points i, j, respectively, J_{ij} Josephson coupling parameter. Namely the Josephson coupling gives rise to the long-range ordering of the phase of the superfluid order parameter in such a multi-center texture. Such a Hamiltonian represents a starting point for the analysis of disordered superconductors, granular superconductivity, insulator-superconductor transition with $\langle i,j\rangle$ array of superconducting islands with phases φ_i, φ_j.

To account for Coulomb interaction and allow for quantum corrections we should introduce into effective Hamiltonian the charging energy[19]

$$H_{ch} = -\frac{1}{2}q^2\sum_{i,j} n_i (C^{-1})_{ij} n_j\,,$$

where n_i is a number operator for particles bound in i-th micrograin; it is quantum-mechanically conjugated to φ: $n_i = -i\partial/\partial\varphi_i$, $(C^{-1})_{ij}$ stands for the capacitance matrix, q for a particle charge.

Such a system appears to reveal a tremendously rich quantum-critical structure. In the absence of disorder, the $T = 0$ phase diagram of the multigranular system implies either triangular, or square crystalline arrangements with possible melting transition to a liquid. It should be noted that analogy with charged $2D$ Coulomb gas implies the Wigner crystallization of multigranular system with Wigner crystal (WC) to Wigner liquid melting transition, respectively. Naturally, that the additional degrees of freedom for micrograin provide a richer physics of such lattices. For a system to be an insulator, disorder is required, which pins the multigranular system and also causes the crystalline order to have a finite correlation length. Traditional approach to a Wigner crystallization implies the formation of a WC for densities lower than a critical density, when the Coulomb energy dominates over the kinetic energy. The effect of quantum fluctuations leads to a (quantum) melting of the solid at high densities, or at a critical lattice spacing. The critical properties of a two-dimensional lattice without any internal degree of freedom are successfully described applying the BKT theory to dislocations and disclinations of the lattice, and proceeds in two steps. The first implies the transition to a liquid-crystal phase with short-range translational order, the second does the transition to isotropic liquid. For such a system provided the micrograin positions fixed at all temperatures, the long-wave-length physics would be described by an antiferromagnetic XY model with expectable BKT transition and gapless XY spin-wave mode.

The low temperature physics in a multigranular system is governed by an interplay of two BKT transitions, for the U(1) phase and positional degrees of freedom, respectively.[21] Dislocations lead to a mismatch in the U(1) degree of freedom, which makes the dislocations bind fractional vortices and lead to a coupling of translational and phase excitations. Both BKT temperatures either coincide (square lattice) or the melting one is higher (triangular lattice).[21]

Quantum fluctuations can substantially affect these results. Quantum melting can destroy U(1) order at sufficiently low densities where the Josephson coupling becomes exponentially small. Similar situation is expected to take place in the vicinity of structural transitions in a multigranular crystal. With increasing the micrograin density the quantum effects result in a significant lowering of the melting temperature as compared with classical square-root dependence. The resulting melting temperature can reveal an oscilating behavior as a function of particle density with zeros at the critical (magic) densities associated with structural phase transitions.

In terms of our model, the positional order corresponds to an incommensurate charge density wave, while the U(1) order does to a superconductivity. In other words, we arrive at a subtle interplay between two orders. The superconducting state evolves from a charge order with $T_C \leq T_m$, where T_m is the temperature of a melting transition which could be termed as a temperature of the opening of the insulating gap (pseudo-gap!?).

The normal modes of a dilute multigranular system include the pseudo-spin waves propagating in-between the micrograins, the positional fluctuations, or quasi-phonon modes, which are gapless in a pure system, but gapped when the lattice is pinned, and, finally, fluctuations in the U(1) order parameter.

The orientational fluctuations of the multigranular system are governed by the gapless XY model.[20] The relevant model description is most familiar as an effective theory of the Josephson junction array. An important feature of the model is that it displays a quantum-critical point.

The low-energy collective excitations of multigranular liquid includes an usual longitudinal acoustic phonon-like branch. The liquid crystal phases differ from the isotropic liquid in that they have massive topological excitations, *i.e.*, the disclinations. One should note that the liquids do not support transverse modes, these could survive in a liquid state only as overdamped modes. So that it is reasonable to assume that solidification of the skyrmion lattice would be accompanied by a stabilization of transverse phonon-like modes with its sharpening below melting transition. In other words an instability of transverse phonon-like modes signals the onset of melting. The phonon-like modes in skyrmion crystal have much in common with usual phonon modes, however, due to electronic nature these can hardly be detected if any by inelastic neutron scattering.

A generic property of the positionally ordered

skyrmion configuration is the sliding mode which is usually pinned by the disorder. The depinning of sliding mode(s) can be detected in a low-frequency and low-temperature optical response.

It should be noted that as regards the CF fluctuations, there is no principal difference between the contributions of real phonon modes and quasi-phonon modes of a multigranular system. Moreover, it is worth noting that the charge inhomogeneity in a multigranular system is proned to be closely coupled with lattice structural distorsions. However, the stabilization of transverse phonon-like modes in multigranular system that accompanies its solidification at the temperatures above T_c may strongly affect the CF relaxation due to a mechanism identical to that of proposed by Lovesey and Staub (magnetoelastic mechanism). In a sense, such a conclusion reconciles "old" spin-fluctuation[1,2] and "new" phonon[15,16] approaches to the INS spectroscopy of cuprates with R-ions.

Concluding we argue that the crystal-field fluctuations induced by the dynamic charge inhomogeneity in copper-oxygen subsystem may be one of the main origin of the broadening of the linewidth of CF transitions for 4f ions in high-T_c cuprates providing the detection of a charge rearrangement accompanying the approach to T_c.

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