How Ice enables Superconductivity in $Na_xCoO_2.yH_2O$ by melting charge order: Possibility of novel Electric Field Effects

G. Baskaran
The Institute of Mathematical Sciences
C.I.T. Campus, Chennai 600 113, India

Charge ordering in doped CoO_2 planes near the commensurate fillings $x = \frac{1}{4}$ and $\frac{1}{3}$ are considered for $Na_xCoO_2.yH_2O$ and suggested to be competitors to superconductivity, leading to the experimentally seen narrow superconducting dome bounded by commensurate doping: $\frac{1}{4} < x < \frac{1}{3}$. Intercalated hydrogen bonded H_2O network, by its enhanced dielectric constant, screen and frustrate local *charge order condensation energy* and replace a generic 'charge glass order' by superconductivity in the dome. An access to superconductivity and charge order, available through the new water channel, is used to predict novel effects such as 'Electrical Modulation of Superconductivity' and 'Electroresistance Effect'.

Discovery of superconductivity in $Na_xCoO_2.yH_2O$ by Takada and collaborators [1] have opened the possibility of realizing unconventional superconductivity and novel quantum states in 2D arising from strong electron correlations in doped CoO_2 layers. Water of a right proportion ($y \approx \frac{4}{3}$) seems absolutely necessary [2–5] for stabilizing superconductivity, suggesting H_2O's critical role. While water does wonders in nature, its key role here is some what puzzling. Elucidating its role in this unusual superconductor is an important task from material science and physics point of view. This is what the present paper attempts using phenomenological and theoretical considerations.

Enthused by the remarkable discovery of superconductivity in $Na_xCoO_2.yH_2O$, the present author [6] and others [7] have suggested a single band t-J model as an appropriate model to understand superconductivity and low energy electronic phenomena. A phase diagram has been suggested using ideas of resonating valence bond (RVB) theory developed for cuprates [8]. A recent experiment [3] which shows superconductivity in a rather narrow range of doping $\frac{1}{4} < x < \frac{1}{3}$, than predicted by RVB theories, suggest that there are perhaps left out interactions and consequent competing phases which make a simple t-J model valid only for limited range of x. The situation is not unusual - even in cuprates a simple t-J modeling is strictly valid only in the neighborhood of optimal doping. Charge order phenomenon [9,10] is known in cuprate superconductors; and it has been suggested to compete [11] with superconductivity.

Doped CoO_2 , compared to CuO_2 layers of high T_c cuprates, has a narrower conduction band and a less polarizable valence band of oxygen. Consequently, short range coulomb repulsions among carriers are screened less. This is likely to stabilize a variety of frustrated charge ordering in the triangular lattice, as we discuss in this paper. NMR result of Ray et al. [12] indeed provides a first evidence for charge freezing in Na_xCoO_2 family ($x = \frac{1}{2}$), $Na_{0.5}CoO_2$ below about $T \approx 300K$, a large temperature scale.

We estimate and include unscreened short range coulomb interactions in the t-J model for the study of unhydrated Na_xCoO_2 . We show that in addition to superconductivity, charge ordering in the narrow conduction band of CoO_2 layer is a major instability, for a range of higher doping than suspected (Wen et al. in ref 7). As the unscreened near neighbor coulomb interactions are large and comparable to the band width, the characteristic charge order temperatures are $T_{\mathrm{ch}} \sim 400K$.

Fortunately, H_2O , in hydrated $Na_xCoO_2.yH_2O$, makes t-J modeling valid for a range of doping. For reasons which we elaborate in the present paper, hydrogen bonded H_2O dipoles of the ice layers screen and frustrate *charge order condensation energy*. That is, they *effectively screen out short range repulsions*, and enable the physics of a simple t-J model to be realized in a narrow range of doping, $\frac{1}{4} < x < \frac{1}{3}$, as superconductivity.

We discuss few important charge ordered states at commensurate fillings, $x = \frac{1}{4}$ and $\frac{1}{3}$, which we believe are competitors to the experimentally observed superconductivity, in the range $\frac{1}{4} < x < \frac{1}{3}$. These reference charge ordered states are strongly frustrated by the random potential from the neighboring Na layers, resulting in a glassy phase in the region $\frac{1}{4} < x < \frac{1}{3}$ and beyond. The charge glass phase is likely to be an anomalous metal, very much like the spin gap phase in cuprates, where there are local charge order activities at low frequency scales.

We estimate the enhancement of the background static dielectric constant at short distance due to hydrogen bonding in the H_2O layers. We find that this screening is sufficient to reduce the large charge order transition temperature down to $\sim 1K$ and allow superconductivity to emerge. Strong commensurability effects and the associated short range charge order reduce superconducting T_c considerably as we approach the commensurate ends $x = \frac{1}{4}$ and $\frac{1}{3}$.

As H_2O stabilize superconductivity and discourages charge order, we have a new access to the electronic phases of CoO_2 layer through water. This leads to the possibility of some novel effects: i) 'Electrical Modulation of Superconductivity' by external electric field or microwave radiation and ii) 'Electroresistance Effect' in the normal state. We estimate that voltages $\sim 500V$, applied capacitively to thin films of $Na_xCoO_2.yH_2O$ of thickness $\sim$ 1 micron will orient the water dipoles and reduce the short distance dielectric screening, resulting in stabilization of charge glass order phase and destabilization of superconductivity. This interesting switching effect may have device potential.

Recently we modeled the low energy physics of doped CoO_2 using a t-J model and discussed an RVB scenario for superconductivity including a PT violating $d_1 + id_2$ wave superconductivity and a $p_1 + ip_2$ wave superconductivity at a higher doping. To study charge order we must include some leading short distance carrier-carrier and carrier-Na-ion screened coulomb interaction:

$$H_{\rm tJV} = -t\sum_{\langle ij\rangle} C^{\dagger}_{i\sigma}C_{j\sigma} + H.c. + J\sum_{\langle ij\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{1}{4}n_i n_j)$$
$$\sum_{ij} V_{ij}(n_i-1)(n_j-1) + \sum_i \epsilon_i(n_i-1) \quad (1)$$

Here C's and $\mathbf{S}$'s are the electron and spin operators. As we have an electron doped system we have the 'zero occupancy' constraint $\sum_\sigma n_{i\sigma} \neq 0$ at every site i.

Recall that doubly occupied Co^{3+} sites carry a charge $-e$ with reference to the neutral CoO_2 layer and V_{ij} is the screened coulomb repulsion between them. We have ignored the small two body off-diagonal coulomb interaction terms. For practical purposes only the nearest and next nearest neighbor terms $V_1 \approx \frac{e^2}{\varepsilon_{ab}R_{nn}}e^{-\frac{R_{nn}}{\lambda_{ab}}}$ and $V_2 \approx \frac{e^2}{\varepsilon_{ab}R_{nnn}}e^{-\frac{R_{nnn}}{\lambda_{ab}}}$ are important. Here $\varepsilon_{ab} \approx \varepsilon_O + \varepsilon_{\rm H_2O}$ represents the short distance dielectric screening arising from the filled oxygen bands of CoO_2 layers and H_2O layers in $Na_xCoO_2.yH_2O$. And $\lambda_{ab} \approx Co-Co$ distance is the Thomas Fermi screening length for our tight binding metallic layer. The random site energy ϵ_i of charge degree of freedom represents the screened coulomb attraction from neighboring Na^+ ions.

Electronic structure calculations [13] give a value of $t \approx -0.1\ eV$ for the conduction band of the CoO_2 layer. We estimate V_1 and V_2 for Na_xCoO_2 , the non-hydrated case. The dielectric constants of oxides of Fe and Ni that flank Co in the periodic table are $\sim$ 4 to 12. We assume a background (short distance) static dielectric constant of $\varepsilon_{ab} \approx 8$ for our CoO_2 layer. Recall that in cuprates the background ϵ is large ~ 20, in view of a more polarizable octahedral oxygen network; in CoO_2 the oxygen filled band is less polarizable and relatively deep below the fermi level. Using this dielectric constant and values of Co-Co distances in $Na_{0.5}CoO_2$ we get $V_1 \approx 0.8\ eV$ and $V_2 \approx 0.4\ eV$. The mean square fluctuation of the carrier site energy due to disordered Na-ions is $\sqrt{\langle\delta\epsilon_i^2\rangle} \approx 0.2\ eV$

In the absence of hopping, the dopant carriers Co^{3+} will order classically and undergo order-disorder transition at a fairly high temperature $k_B T_{\rm ch}(\text{classical}) \approx 2\bar{\rm V} \sim 10^3$ K; here $\bar{V} \equiv \frac{1}{2}(V_1 + V_2)$ is a mean short distance repulsion. However the electron dynamics reduce $T_{\rm ch}$(classical) considerably. To estimate this reduction we perform a mean field analysis of the t-J-V model for a CDW order, pretending that an unfrustrated charge order arises from nesting instability for $Na_{0.5}CoO_2$. This gives us a BCS like expression for T_c :

$$k_B T_{ch} \approx \epsilon_F e^{-\frac{1}{\bar{V}\rho_o}} \quad (2)$$

Here ρ_o is a fermi sea averaged particle-hole density of states corresponding to the ordering wave vector. Substituting $\epsilon_F \approx 0.5\ eV$, $\rho_0 \approx \frac{1}{2\epsilon_F}$ and $\bar{V} \approx 0.4$, we get $T_{\rm ch} \approx 480K$. Frustration on the triangular lattice at half filling and disorder effect from Na ions will further reduce this. Thus we get a charge order temperature in the right range, $T_{\rm ch}(NMR) \approx 300\ K$, seen in NMR,

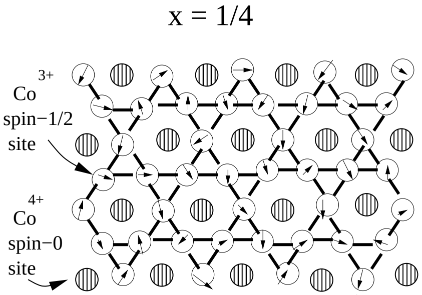

FIG. 1. 'Classical' charge order for $x = \frac{1}{4}$. Spin-0, charge $-e$ carriers (Co^{3+}) form a triangular lattice. Neutral sites with spin-$\frac{1}{2}$ moments (Co^{4+}) form a Kagome lattice. Quantum fluctuations will reduce the amplitude of charge order substantially. Accompanying charge order, we expect some interesting spin liquid phase or complex short range spin order at low temperatures

Before we consider influence of H_2O we discuss some simple charge orders at $x = \frac{1}{4}$ and $\frac{1}{3}$ that are favored by electrostatics in the unhydrated Na_xCoO_2 . We ignore the superexchange contribution, as $J << V_1, V_2$. For $x = \frac{1}{4}$, the Co^{3+} sites are arranged on a triangular lattice (figure 1) to minimize coulomb repulsions. Interestingly, the remaining sites carry spins and form spin-$\frac{1}{2}$ Heisenberg antiferromagnet on a Kagome lattice. In our convention, the classical energy of this state is $E_{\frac{1}{4}}(\text{Kagome}) = 0$. In the real system, carrier delocalization will considerably reduce the amplitude of charge order. *In this sense the charge ordered states shown in figure 1 and figure 2 are to be thought of as reference classical states.*

Another ground state comparable in energy is an anisotropic metal. It has ordered stripes - alternating insulating and 0.5 electron doped chains. The electrostatic energy of this state per site is $\frac{1}{4}(V_1 + V_2)$. However, the carrier delocalization in the 0.5 electron doped chains leads to a gain in kinetic energy which is easily estimated when J is neglected in our t-J model. This case corresponds to a quarter filled infinite U Hubbard model, which can be converted into a half filled band of non-interacting spinless fermions giving us the delocalization energy $= -|t| \sum \cos k = -2\frac{|t|}{\pi}$. Thus we get a total energy per site, $E_{\frac{1}{4}}(\text{stripe}) = \frac{1}{4}(V_1 + V_2) - 2\frac{|t|}{\pi}$.

Figure 2 shows the case of $x = \frac{1}{3}$. This classical ground state minimizes electrostatic repulsion and Co^{3+} sites fill one of the three sublattices and the remaining hexagonal lattice is the neutral spin-$\frac{1}{2}$ site. It is a hexagonal spin-$\frac{1}{2}$ quantum antiferromagnet. The energy of this state per site is $E_{\frac{1}{3}} = \frac{V_2}{2}$. We also find striped states which are local minima.

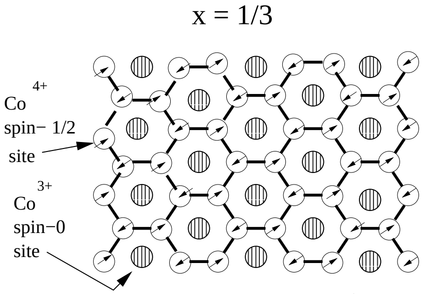

FIG. 2. 'Classical' charge order for $x = \frac{1}{3}$. Triangular lattice of localized charge $-e$ carriers and a Hexagonal lattice of neutral spin-$\frac{1}{2}$ moments. Quantum fluctuations will reduce the amplitude of charge order substantially. Accompanying charge order we expect short range AFM order at low temperatures

So far we studied charge order in the CoO_2 plane at commensurate fillings. As we move away from $x = \frac{1}{3}$ and $x = \frac{1}{4}$, defects and discommensurations will be produced or we may go to an incommensurate charge ordered structure. There may be one or more first order phase boundary between $x = \frac{1}{3}$ and $x = \frac{1}{4}$. However, all these nice charge ordered phases will be challenged by a generically disordered arrangement of Na ions in a triangular lattice and the consequent random potential seen by the mobile Co^{3+} carriers as explained below .

The energetically preferred sites of Na atoms [14] in Na_xCoO_2 form a triangular lattice that have the same lattice parameter as the triangular Co layer. However, the Na and Co lattices are relatively shifted - if we project the allowed positions of the Na atoms of the nearest top and bottom layer onto the Co layer, these sites become the dual lattice (hexagonal lattice) of the Co triangular lattice. Because of this *a sublattice order of the Na atoms does not couple to the charge density wave order-parameter of the CoO_2 lattice and in principle allows a finite temperature charge order-disorder phase transition*: a 3-state Potts (Z_3 symmetry) model transition at $x = \frac{1}{3}$ and a 4-state Potts model (Z_4 symmetry) transition at $x = \frac{1}{4}$. However, an inevitable disorder in Na sublattice leads to, based on an Imry-Ma type of argument, a glassy order at low temperatures rather than a genuine charge order phase transition. Thus we expect a phase diagram depicted in figure 3 for the range $\frac{1}{3} < x < \frac{1}{4}$.

Let us move on to the hydrated case, $Na_xCoO_2.yH_2O$. As we mentioned earlier, the enhanced dielectric constant of the H_2O layer will screen short range coulomb repulsion and weaken and melt the high temperature charge ordering. It also screens and weakens the random Na potential seen by the carriers. For the appearance of low temperature superconductivity T_{ch} need not be reduced to nearly zero value. A sufficiently weakened charge ordered state may give up at low temperatures and superconductivity may emerge. Figure 3 shows sketches the change of phase diagram as we go to the hydrated case. A strong resistance anomaly seen in a recent experiment [5] at $T^* \approx 50\ K$, may be the weakened charge order transition that we are discussing.

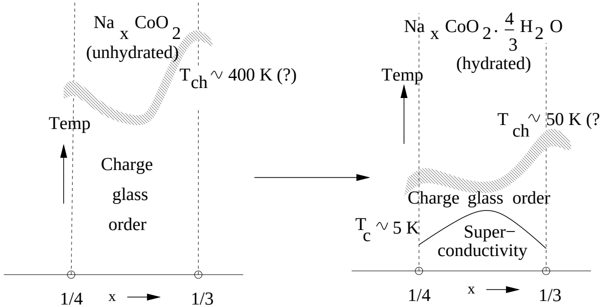

FIG. 3. Schematic phase diagram showing how hydration affects electronic phases: superconductivity is stabilized at low temperatures by a strong suppression of charge glass order.

Let us discuss nature of H_2O ordering hydrogen bonding in $Na_xCoO_2.yH_2O$ in some detail. In what follows we use a recent suggestion of Cava et al. [15] that H_2O may have a structure similar to the layers in hexagonal ice (1h ice). As mentioned earlier, in Na_xCoO_2 , energetically favorable interlayer sites of Na form a triangular lattice. These sites are at the center of trigonal biprisms, capped by an oxygen atom at the top and one at the bottom. To understand H_2O ordering, we consider $Na_{\frac{1}{3}}.CoO_2.\frac{4}{3}H_2O$ as a reference compound. Fill one of of the three sublattices by Na atoms to minimize electrostatic energy. We are left with two empty sublattices that form a hexagonal lattice. Two H_2O molecules may be accommodated at the top and bottom of the capped trigonal biprism. By doing so we get two hexagonal lattices of H_2O sandwiching a triangular lattice of Na ions. Thus we have a triangular lattice filled by Na and H_2O in the ratio $1:4$. We can view the above hexagonal sheets as the sheets in hexagonal ice structure, as suggested by Cava and collaborators [15] in their preliminary studies. *We find it very interesting that the nearest neighbor H_2O-H_2O distance in the above geometry,* ≈ 2.81 *Au, is nearly the same [16] as that in real hexagonal ice* ≈ 2.71. No wonder water may freeze into ice in $Na_xCoO_2.yH_2O$! Having nearly the same H_2O -H_2O distance may also help ice sheets to have a good hydrogen bonding network like in hexagonal ice.

Thus it is likely that H_2O molecules continue to have hydrogen bonding in spite of the CoO_2 and Na environment. As hydrogen bond energy is substantial $\sim 0.5\ eV$, water tends to have hydrogen bonding activity in extreme environments. Examples are biological systems, clathrate hydrates and water containing charged ions, where H_2O continue to maintain hydrogen bonding even though the local structure deviates considerably from the standard ice or water structure. Further the random Na environment in $Na_xCoO_2.yH_2O$ may convert the 2D ice layer into a 2D amorphous ice layer with a good short range hexagonal order.

Now we discuss how the dielectric property of the H_2O layer may control the low temperature electronic phases of the conducting CoO_2 layer. We are interested in finding how the electron-electron interactions at the charge order wave vector $\mathbf{q} = \mathbf{Q}$ get screened by the interacting water dipoles. The relevant static dielectric constant is $\epsilon_{\rm H_2O}(Q)$. In an ice system like ours with a large disorder in dipole orientations, we expect very small variation of $\epsilon_{\rm H_2O}(q)$ with q. Further random site disorder in the Na sublattice will produce Bjerrum defects; so we do not expect a 2D dipolar order-disorder transition, as in ideal 2D models of ice.

Dielectric constant of ice has been studied extensively in the past and also recently [17,18,16]. A general expression for the dielectric constant of an interacting dipolar system is [17,18]:

$$\epsilon = \epsilon_\infty + \frac{4\pi}{3Vk_BT}\langle(\mathbf{P} - \langle\mathbf{P}\rangle)^2\rangle \tag{3}$$

Here $\epsilon_\infty \sim 1-2$ is the high frequency dielectric constant of the dipole, in our case H_2O molecule. $\mathbf{P}$ is the total dipole moment of the system of volume V. And $\langle\ ...\ \rangle$ denotes thermal average. Static dielectric constant of ice has not been measured at liquid He temperatures, as the dielectric relaxation becomes too slow even around liquid air temperatures. Fortunately, extensive numerical study of $\epsilon_{\rm H_2O}$ are available. For example, a recent calculation [18] shows that for hexagonal ice, $\epsilon_{\rm H_2O} \approx 220$ at $T = 50K$.

We use this 3D result to get an approximate estimate for our weakly coupled hexagonal ice layers as follows. We replace the volume V by $\approx 6V$ to account for the c-axis expansion in $Na_xCoO_2.yH_2O$. Missing hydrogen bonds along the c-axis reduces the number of allowed proton configurations leading to a reduction of $\langle(\mathbf{P} - \langle\mathbf{P}\rangle)^2\rangle$ to $\approx \frac{2}{3}\langle(\mathbf{P} - \langle\mathbf{P}\rangle)^2\rangle$. This gives us $\epsilon_{\rm H_2O}$ (hexagonal sheet) ≈ 20 at $T = 50K$. Our system being strongly disordered, we do not expect $\epsilon_{\rm H_2O}$ (hexagonal sheet) to change at lower temperatures. Thus the background dielectric constant of $Na_xCoO_2.yH_2O$ is $\epsilon = \epsilon_o + \epsilon_{\rm H_2O} \approx 8 + 20$. This reduces the mean short range repulsion by nearly a factor of 3, making the $T_{\rm ch} \approx 1K$, in equation (2). Once the long range charge order is disabled by a reduction of V, the simple t-J model and consequent low temperature superconducting phase is realized, albeit with a reduced T_c in the range $\frac{1}{3} < x < \frac{1}{4}$. The sharp reduction in superconducting T_c at the commensurate boundaries of the dome should arise from the strong short range order and lesser discommensurations and defects. The experimentally seen flat value of $T_c \approx 2K$ for $x < \frac{1}{4}$ and for $x > \frac{1}{3}$is likely to be an effect of phase separation.

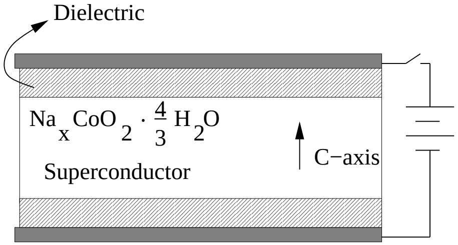

FIG. 4. Schematic experiment to observe the ‘Electrical Modulation of Superconducitivy’. The order voltage required is 500 V, when the film thickness is about a micron.

Our proposal of a critical and catalytic role of H_2O layer suggests ways to access and control low temperature electronic phases of the CoO_2 layer. Based on this we suggest two effects: i) ‘Electrical Modulation of Superconductivity’. Here we control (figure 4) superconductivity and superconducting T_c by modifying the screening property of H_2O layer by external electric fields - DC, AC or pulsed fields. This has interesting consequences of being able to locally erase superconductivity by STM tips, dynamically create Josephson networks or create 2D superconductivity of desired shapes through appropriate capacitor shapes etc. Since microwaves are absorbed by hydrogen bonded networks we can pump microwaves at appropriate frequencies ($\hbar\omega < \Delta_{\rm sc}$, the superconducting gap) and dynamically polarize water dipoles and may influence its dielectric properties, and in turn control superconductivity.

ii) ‘Electroresistance Effect’. By modifying the amplitude of charge glass order as well as $T_{\rm ch}$ in the non-superconducting state, by influencing the H_2O layer by external DC or AC electric field, we can change ρ_{ab}, the ab-plane resistivity.

Below we estimate the electric field required to completely suppress superconductivity. Having established a hydrogen bonded network it requires a finite energy to rotate a water molecule and orient its dipole moment along an external electric field. In infrared absorption and neutron scattering experiments [16] the absorption band corresponding to rotation of H_2O molecules is in the range 60 to 120 meV. Assuming a random orientation, the average energy required to reorient a water molecule is $\approx 50\ meV$, i.e., a potential of 50 mV applied over the length $\approx 1\ Au$ of the water dipole will orient the dipole moment of water along its field. If we have c-axis oriented $Na_xCoO_2.yH_2O$ film of thickness 1 micron we need to apply a voltage $\approx 500\ Volts$ across the film, in order to orient the majority of dipoles. Strong polarization of water dipoles reduces the dielectric constant, as is evident from equation (3). The resulting reduced screening of carriers in the CoO_2 layer allows charge order to grow and superconductivity gets suppressed.

A theoretical analysis, including some of the possible difficulties in observing the effects will be presented in a future publication.

To get a clear understanding of this complex system, and to see if our proposal is correct more experiments are necessary:

a) **Charge Order:** It will be interesting to perform NMR, NQR, STM, μSR and other local probe measurements to look for charge order in the vicinity of the commensurate fillings $x = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$ and $\frac{3}{4}$ and see how they differ between the two systems $Na_xCoO_2.yH_2O$ and Na_xCoO_2 .

b) **Spin order, singlets and gaps:** Accompanying local charge order we expect a spin order at low temperatures (the scale of J is small, $\sim$ 6 to 7 meV). In general the enhanced singlet stabilization by the superexchange process will introduce some kind of spin gap phenomenon. If the charge order at $x = \frac{1}{4}$ leads to a Kagome lattice of spins it will be an interesting testing ground for some of the ideas of the spin liquid phase of spin-$\frac{1}{2}$ Kagome antiferromagnet, including possible novel excitations.

c) **Lower Doping:** Experimentally, it has not been possible [3] to make $Na_xCoO_2.yH_2O$ for $x < \frac{1}{4}$. It is likely [3] that c-axis ionic bonding is weakened, by decreasing x and presence of water layer, making a 3D structure unstable. It will be important to synthesize, by non-equilibrium means, meta stable compounds for $x < \frac{1}{4}$ to test the validity of RVB theory and also test our hypothesis of the role played by water.

d) **Replacing H_2O :** It will be desirable to have a stable solid $Na_xCoO_2.yX$, where an intercalant 'X' not only increases the dielectric constant but also provides additional bonding between CoO_2 layers and make stable compounds for $x < \frac{1}{4}$.

e) **Higher doping:** According to reference 6, the dopant induced dynamics, within the t-J model will favor ferromagnetic correlations and a consequent p-wave superconductivity at higher dopings slightly above $x = \frac{1}{3}$. It will be interesting to look for this.

f) **Inhomogeneous Superconductivity:** If ice plays a central role, as suggested in this paper, H_2O density fluctuation in ice layer will directly influence superconductivity in nearby CoO_2 layers resulting in a corresponding fluctuation in the superconducting order parameter and possible well grown local charge ordered phase.

g) **Slow Relaxation:** Since interacting water dipoles have very slow dielectric relaxation time scales [16], they may consequently affect superconductivity and impose some anomalous relaxation/aging effects.

The present paper is phenomenological and qualitative in character. Any detailed quantitative calculations of T_c and phase diagram for this complex system needs further experimental guidance. Issue of calculating local screening and dielectric constant in hydrogen bonded systems is known to have subtleties; added to this, we have conducting layers sandwiching water layers. We have made very crude estimates based on simple physical arguments and very approximate considerations, as our primary aim is to focus and identify how water could play a crucial role in this complex system.

We thank A.K. Mishra, V.N. Muthukumar, Debanand Sa, Manas Sardar and R. Shankar for discussion and Latha Malar Baskaran for reference [18].

---

[1] K. Takada et al., Nature, **422** 53 (03)
[2] M. Foo et al., cond-mat/0304464
[3] Y. Wang et al., cond-mat/0305455
[4] B. Lorenz et al., cond-mat/0304537; F. Rivadulla et al., cond-mat/0304455
[5] R. Jin et al., cond-mat/0306066
[6] G. Baskaran, cond-mat/0303649
[7] Brijesh Kumar, B.S. Shastry, cond-mat/0304210; Qiang-Hua Wang, Dung-Hai Lee and Patrick A. Lee, cond-mat/0304377; Masao Ogata, cond-mat/0304405
[8] P.W. Anderson, Science, **235** 1196 (87) G. Baskaran, Z. Zou and P.W. Anderson, Sol. St. Commn, **63** 973 (87); G. Baskaran and P.W. Anderson, Phys. Rev. **B 37** 580 (88)
[9] J. Zaanen and O. Gunnarsson, Phys. Rev. **B 46** 7391 (89); V.J. Emery, S. A. Kivelson and O. Zachar, Phys. Rev. **B 56** 6120 (97); S.R. White and D.J. Scalapino, Phys. Rev. **B 60** R753 (99);
[10] J.M. Tranquada et al., Nature **375** 561 (95)
[11] G. Baskaran, Mod. Phys. Lett., **B 14** 377 (00)
[12] R. Ray et al., Phys. Rev. **B 59** 9454 (99); Phys. stat. sol. **B 215** 703 (99)
[13] D.J. Singh, Phys. Rev. **B 61** 13397 (00)
[14] R.J. Balsys and R.L. Davis, Sol. St. Ionics, **93** 279 (96)
[15] R. Cava, M2S-Rio Meeting, 25-30 May 2003.
[16] V. F. Petrenko and R. W. Whitworth, Physics of Ice, (Oxford University Press, 1999)
[17] H. Frohlich, Theory of Dielectrics and Dielectric Loss (Oxford University Press, Oxford, 1958)
[18] S.W. Rick and A.D.J. Haymet, J. Chem. Phys. **118** 9291 (2003)