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producida por M.D.Nuñez Regueiro y A.A. Aligia

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COMMON EXCITONIC MECHANISM FOR CuO_2 AND BiO_3 BASED PEROVSKITES

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Abstract: BiO_3-based high Tc oxides are studied and compared to CuO_2 based ones. Both are described by a general Hamiltonian and studied by perturbation theory in the hopping energy. It is shown that a common polarization mechanism can give rise to pairing of the O holes added to the antiferromagnetic or disproportionated semiconducting states. The necessary conditions are: proximity of the M(Cu or Bi) and O levels, a gap in the electronic spectrum of the system and important nearest-neighbor M-O repulsion.

The recent discovery of the high Tc superconductors Ba_{1-x} (K or Rb)$_x BiO_3$ [1]- closely related to $BaPb_{1-x}Bi_xO_3$ [2]-raises the question of whether the mechanism of superconductivity in this new family is similar to the one present in the CuO_2 based compounds. A first comparison shows that their main common property is a similar type of O-metal network, which as evidenced by the existence of O holes in the cuprates[3], is relevant for superconductivity. On the other hand, in both cases the undoped compounds are insulators while doping leads to anomalously high superconducting transition temperatures Tc, with a low number of carriers. This would imply that both the bismuth and copper oxides should be explained by a common mechanism.

For the cuprates a broad consensus has emerged that phonons alone cannot be responsible for the phenomenon, and different non-phonon models have been proposed[4]. Between them, those based on magnetic fluctuations seem not to be simply transferable to these new compounds without magnetic ions. In contrast, we show that a similar excitonic mechanism can give rise to pairing of the O holes in both families. The necessary conditions for

this mechanism are discussed analysing both types of oxides within perturbation theory in the hopping t. We compare our results with those of small cluster calculations[5], arriving to similer conclusions. The same model with parameters appropriate for $BaBiO_3$ yields a disproportionated insulating ground state and attraction between O holes with doping.

We represent both types of systems by a simple cubic lattice of metal ions (M = Cu or Bi) in d dimensions (d = 2,3), with an O ion between any two M ions. A common Hamiltonian describing the dynamics of the holes is:

$$H = H_o + H'$$

$$H_o = \sum_{ijk\sigma} \left\{ \varepsilon_M + A \sum_{<\ell>} S_\ell (-1)^{i+j+k} \right\} n^M_{ijk\sigma} + \sum_{\ell\sigma} \varepsilon_p \, n^p_{\ell\sigma} +$$

$$+ U_M \sum_{ijk} n^M_{ijk\uparrow} \, n^M_{ijk\downarrow} + U_p \sum_{\ell} n^p_{\ell\uparrow} \, n^p_{\ell\downarrow} +$$

$$+ \sum_{ijk\sigma} \sum_{<\ell>} \left\{ G - \frac{A}{2} S_\ell (-1)^{i+j+k} \right\} n^M_{ijk\sigma} \, n^p_{\ell\sigma'} + \sum_{\ell} B S^2_\ell$$

$$H' = t \sum_{ijk\sigma} \sum_{<\ell>} \left[c^{M+}_{ijk\sigma} \, p_{\ell\sigma} + h.c. \right) \qquad (1)$$

ij(k) labels the M positions, ℓ the O sites. The first term in H_o represents the energy of the M orbitals ($3d(x^2-y^2)$ if M = Cu, 6s if M = Bi). The second is the energy of the O p orbitals directed to their nearest-neighbor M ions. The third and forth terms describe on-site Coulomb energies, the fifth represents the intersite Coulomb repulsion between M and O ions. The last term of H_o accounts for the elastic energy loss when O atoms are displaced along the nearest-neighbors line. Each displacement modifies the on-site and intersite energies of the two neighboring M ions in an apposite way. We consider only three positions for the O ions, $S_\ell = 0, \pm 1$. We also assume $A<B<2A$. $S_\ell = 1(-1)$ for all ℓ corresponds to a breathing distortion. H' represents the hopping between nearest neighbor M and O ions.

This Hamiltonian contains and unifies the models proposed by Varma et al.[6] and studied by Hirsch et al. and Balseiro et al.[5]- in which there are no O displacements- and by Rice and Sneddon[7]- in which O levels are

neglected-. As correlations are essential, we solve the interaction Hamiltonian H_o exactly and include H' as perturbation. We define:

$$\Delta = \varepsilon_p - \varepsilon_M \quad ; \quad \tilde{U} = U_M - Z(2A-B) \tag{2}$$

where Z = 2d is the coordination number of the M ions. Assuming for the moment $\Delta > 0$, the ground state of H_o for the undoped compounds depends on the sign of $\tilde{U}$. If $\tilde{U} > 0$ the ground state has one hole in each M ion and the O ions are undistorted. If instead $\tilde{U} < 0$ a disproportionation accompanied by a breathing mode distortion takes place and the ground state consists of alternating doubly occupied and empty metal sites, $\tilde{U}$ acts as an effective on-site attraction for half of the M sites. We believe that in layered Cu oxides, $\tilde{U} > 0$, while in $BaBiO_3$ based compounds, due to the larger dimensionality (Z = 6) and the lower magnitude of the s-s intra-atomic Coulomb repulsion compared to the d-d one, $\tilde{U} < 0$. This is also consistent with the breathing mode observed in $BaBiO_3$[2] but not in the Cu-based compounds.

We first consider the Cu-based oxides for which $\tilde{U}$ and $\Delta > 0$. Details of the calculations and the second order energies of the different possible states of H_o when one or two holes are added to the N-holes semiconducting state have been given elsewhere[8]. Here we summarize the results. Fig.1 shows for Z = 4 the resulting binding energy defined as:

$$E_b = E(N+2) - 2E(N+1) \tag{3}$$

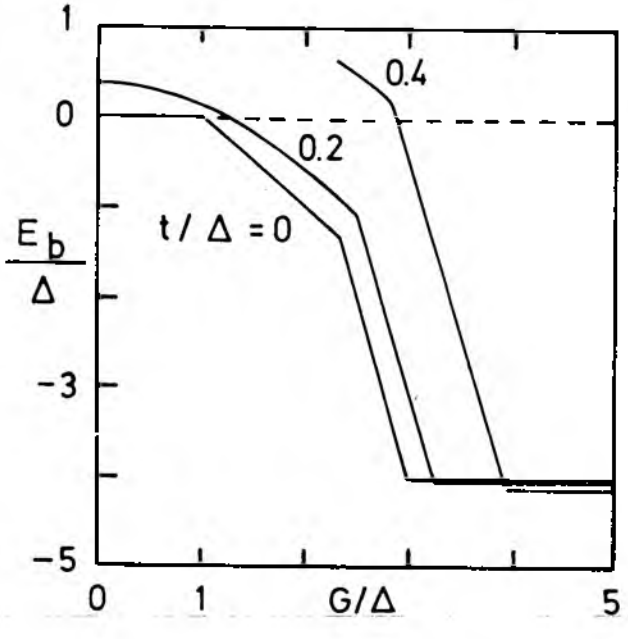

FIG. 1- Binding energy defined by Eq. 3 as a function of G for $U_M, U_p \to \infty$, d = 2 and indicated values of t/Δ.

The results are in qualitative agreement with numerical calculations[5]. For U_p and $U_M \to \infty$ an attraction between O holes occurs for large enough G, the critical value G^c, decreasing with Δ, $G^c/\Delta \to 0.54 + 0.07\ (3-Z/2)$ when $t \to 0$.

The key of the pairing mechanism between O holes is that when the second hole is added sufficiently near to the first, a reorganization of the charges, lowering the total energy becomes possible. A similar process cannot take place if in the ground state for N+2 holes, only M sites are occupied. This leads to a minimum U_M for excitonic pairing. For $t \to 0$ we obtain $U_M^c/\Delta \to 2.42+0.15(3-Z/2)$. The interval of G for which $E_b < 0$ shrinks when U_M decreases. For $t = 0$ and $U_M < 5\Delta$, $E_b < 0$ only for $G < -\Delta + 2U_M/3$. For finite t this upper bound increases.

Note that while in the undoped compounds, the antiferromagnetic alignement of the M spins is favored by an energy of order $t^4/(\Delta+G)^2U_M$, terms of order $(H')^2$ favor a local ferromagnetic alignement when holes are added; i.e. the antiferromagnetism is progressively destroyed with doping.

For simplicity we have discussed the $U_p \to \infty$ case, for finite U_p pairing of holes on the same O site can also occur by this excitonic mechanism. We have only considered on-site and nearest-neighbor repulsions. Although long range Coulomb energies not present in our Hamiltonian, act against the binding energy, they will also prevent condensation of a large number of O holes in the same region.

We consider now a different range of parameters which we believe correspond to the non magnetic Bi-based compounds:
$\tilde{U}$, Δ, $A'-U_p$ and $E_{BP} < 0$, where:

$$E_{BP} = U_M - 2\Delta - ZA' \quad ; \quad A' = 2A - B \qquad (4)$$

In this case, the undoped ground state corresponds to the distorted disproportionated one proposed for $Ba_2Bi^{3+}Bi^{5+}O_6$ [2]. The added holes go preferentially to the O sites as shown in Fig.2, where the ground state for different values of G is represented. The energy difference between the state with two holes added to a Bi^{3+} ion and that of Fig.2 d) is: $2U_M - 4\Delta$. Taking $\Delta \sim -2.2$eV [9] and $U_M \sim 2$-3eV, this difference is ~13-15eV. Thus, for these parameters, the bipolarons can move only if electrons, but not holes, are added to the system.

The resulting binding energy in order t^2 [8], for Z = 6 is plotted in

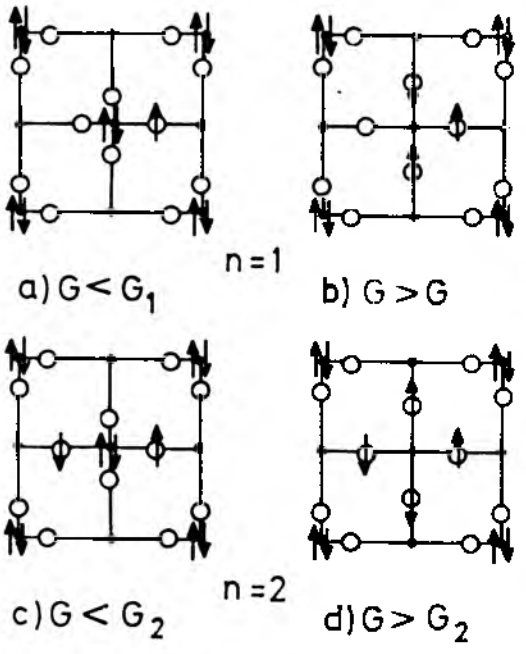

FIG. 2- Schematic representation of the configurations that constitute the ground state for $\tilde{U} < 0$ (Bi oxides) for N+n holes and different values of G. The indicated ranges of G correspond to t=0. Open circles and dots denote oxygen and metal sites respectively.
$G_1 = (|E_{BP}| - A')/2$, $G_2 = G_1 - |E_{BP}|/4$.

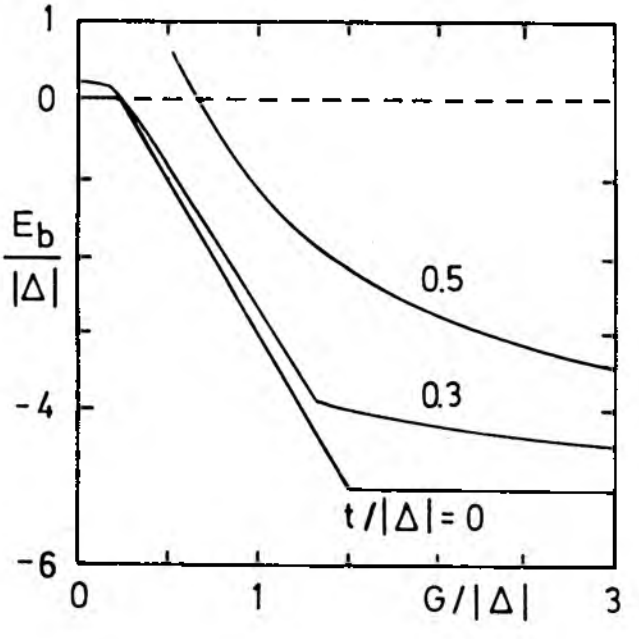

FIG. 3- Binding energy defined by Eq. 3 as a function of G for $\tilde{U}$, $\Delta < 0$, d=3 and indicated values of t/A. The parameters were chosen in the range corresponding to $G_2 > 0$: $U_M = 5|\Delta|$, $U_p = 4|\Delta|$ and $A' = 2|\Delta|$.

Fig. 3. As before, we find attraction between O holes for $G > G^c$. A lower limit of E_b is E_{BP}, i.e. the binding energy of a bipolaron. Excitonic pairing occurs when the ground state for two added holes has the form of Fig. 2(d): the charge reorders breaking a bipolaron at a doubly occupied M site and decreasing the total interatomic Coulomb energy. For t = 0, $G^c = -(E_{BP}+2A')/4$. Terms of order t^4 favor a singlet N+2 holes ground state. This agrees with susceptibility measurements in $Ba_{1-x}K_xBiO_3$ [1].

The compound $BaPb_{1-x}Bi_xO_3$ [2], in which the metal ions themselves are susbtituted, is particulary interesting. Since the Pb valence is equal to the average Bi valence (+4), a small amount of Pb substitution does not provide new carriers to the system and it remains semiconducting. The effect of larger amounts of Pb is twofold: the Pb 6s band broadens and on the other hand, as the number of distorted O ions decreases, the difference of effective on-site energies between the two types of Bi sites, $|E_{BP}|$, G^c and the energy E_2 of the state of Fig. 2d) all decrease. Our view of the

metal-insulator transition is that it happens when the necessary energy to put an electron at the bottom of the Pb 6s band becomes $-E_2/2$. For larger amounts of Pb, but no so large to inhibit the disproportionation completely, the system would show two types of carriers: light Pb 6s electrons and heavy hole-like carriers with a large admixture of structures of the type of Fig.2d). This agrees with Seebeck measurements in this compound[10]. The band structure emerging from this picture is also consistent with optical results as we shall show elsewhere.

To conclude, from a model Hamiltonian including just what are well known features of the insulating parent systems, it has been shown that doping induces pairing between O holes for large enough G, through a common polarization mechanism, inhibiting the spin or charge instabilities. The necessary conditions are: 1) quasidegeneracy of the M and O levels, 2) a gap in the electronic spectrum and 3) large enough repulsion between nearest-neighbor M and O orbitals. This excitonic mechanism involves only one electron-hole pair in the cuprates but two in the bismuth oxides. The mobility of these states is low, it increases with t and decreases strongly with G. For $\tilde{U} < 0$ the mobility of the bipolarons is in any case lower than that of the structures of Fig.2d) as in this latter case due to the larger number of configurations in d=3 there are much more hopping process. Due to the local character of the disproportionation, the O distortion slightly reduces both mobilities. For a typical breathing mode frequency $\omega \sim 15$ THz [11] and a distortion $\delta = 0.08$Å [3], the hopping matrix elements are reduced by only about 5%. Instead, direct O-O hopping and higher Z enhance the mobility. Probably the region relevant to superconductivity is G just above G^c, one has in fact smaller E_b but considerably higher mobility. The effect of pressure, increasing the hopping parameters, will favor the mobility. Although pairing does not necessarily mean superconductivity, our results favor s-wave superconductivity.

References

1) Mattheis L.F., Gyorgy E.M. and Johnson D.W., Phys.Rev.B 37, 3742 (1988); Cava R.J., Batlogg B., Krajewski J.J., Farrow R., Rupp L.W., White A.E., Short K., Peck W.F. and Kometani T., Nature 332, 814 (1988).

2) Cox D.E. and Sleight A.W., Acta Cryst.B 35, 1 (1979).

3) Nücker N., Fink J., Fuggle J.C., Durham P.J. and Temmerman W.N., Phys.Rev.B 37, 5158 (1988).

4) "International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity", Interlaken, Switzerland (1988), Physica C, to be published.

5) Hirsch J.E., Tang S., Loh E. and Scalapino D.J., Phys.Rev.Lett.60, 1668 (1988) and in ref.1); Balseiro C.A., Rojo A.G., Gagliano E.R. and Alascio B., Phys.Rev.B (in press) and in ref.1).

6) Varma C.M., Schmitt-Rink S. and Abrahams E., Solid State Comm.62, 681 (1987).

7) Rice T.M. and Sneddon L., Phys.Rev.Lett.47, 689 (1981).

8) Nuñez Regueiro M.D. and Aligia A.A., submitted.

9) Mattheis L.F. and Hamann D.R., Phys.Rev.B 28, 4227 (1983).

10) Tani T., Itoh T. and Tanaka S., J.Phys.Soc.Jpn.Suppl.A 49, 309 (1980).

11) Pintschovius L., Bassat J.M., Odier P., Gervais F., Hennion B. and Reichardt W., Europhys. Lett.5, 247 (1988).

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SEÑOR DIRECTOR DEL CENTRO ATOMICO BARILOCHE:

De acuerdo con las normas establecidas para la publicación de trabajos (BAP 96/70), elevo para su consideración el trabajo titulado "Common excitonic mechanism for CuO_2 and BiO_3based perovskites".

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De acuerdo a lo establecido en la Resolución de Presidencia N°1018, artículos 4° y 5°, se remite en devolución el presente expediente.

El trabajo titulado: "COMMON EXCITONIC MECHANISM FOR CuO_2 AND BiO_3 BASED PEROVSKITES"

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