Electronically driven instabilities of $La_{2-x}M_xCuO_4$

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Abstract

We study the electronic structure and magnetic and structural instabilities of $La_{2-x}M_xCu\ O_{4-y}$ (M = Sr, Ba) using a tight-binding model and the electron-phonon interaction derived from it. We include both e_g orbitals of Cu atoms and the p orbitals of both unequivalent O atoms. For hopping parameters derived from band structure calculations and Cu intra-atomic Coulomb repulsion $U \lesssim 2.5$ eV, antiferromagnetic instabilities are favoured when the number of electrons in the system is in excess with respect to the stoichiometric compound, while structural instabilities, like a dimerization of Cu atoms, are more likely to occur for electronic defficient compounds, for which the interaction of the electrons with high frequency zone-boundary phonon modes has a maximum as a function of the composition parameter. For $U > 3$ eV, the system is unstable against antiferromagnetism for all compositions of interest.

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1.- Introduction

After the discovery of high T_c superconductivity in $La_{2-x}Ba_xCu\ O_4$ [1], several authors made first principles band-structure calculations of related compounds [2-6]. Although the shape of the Fermi surface obtained in these works differs considerably from one work to another, there is an agreement on the fact that the band that crosses the Fermi energy consists mainly of an antibonding band resulting from hybridization between the Cu 3d orbitals with x^2-y^2 symmetry and the O 2p orbitals which are directed along the Cu-O(2) nearest neighbors distance. Here, as usual, we call x-y the plane perpedicular to the tetragonal axis containing the Cu and O(2) atoms.

Several model Hamiltonians based on these orbitals have been used in the theoretical analysis of high T_c superconductors. These models can be divided in those which assume the Coulomb interactions as the dominant ones, like resonant valence bond [7] or excitonic theories [8,9], and those in which the width of the antibonding band is large enough for the Hartree-Fock approximation to be valid. In this case, the insulating behaviour of La_2CuO_4 is ascribed to some instability of the electronic structure which takes place as a consequence of the perfect nesting of the Fermi surface [10-16]. In most of these works, it was believed that the role of substitution of La by a divalent metal is to remove the nesting condition and with it the instability, allowing for the formation of the superconducting phase through conventional electron-phonon interaction. Nevertheless, it was

shown that superconductivity can coexist with a Peierls distortion[17,18]. While antiferromagnetic order [19-21] and a buckling of the Cu-O(2) planes[13,22,23] was observed, there is no experimental evidence of predicted frozen-in breathing[2,11,16] or Cu dimerization[15] modes.

The controversy about the relative importance of the Coulomb correlations is still open. While a rather important intra-atomic Coulomb interaction between 3d electrons U ~ 6 eV has been estimated by XPS experiments in $YBa_2Cu_3O_7$[24], it has been argued that a consistent picture of transport and superconductivity can be obtained on the basis of band structure calculations and standard electron-phonon interaction[25].

Another controversy concerns the ionic or covalent character of the short Cu-O bond. Experimental studies on plasmons[26] in $La_2Ni\ O_4$ and the short Cu-O distance are in favour of a large covalent character of the bond. Also the Cu $2p_{3/2}$ XPS core level shift display features corresponding to a quantum mixture of Cu^{+2} and a lesser amount of Cu^{+1} ions[27,28] in agreement with the band structure calculations.

In this work we study the spin and charge density instabilities of the system, using a tight binding model in the Hartree-Fock approximation,which includes not only the above mentioned orbitals but also the Cu 3d orbitals with $3z^2-r^2$ symmetry, the O(1) 2_z orbitals and all the hopping integrals involving the shortest Cu-O(1), Cu-O(2), O(2)-O(2) and O(1)-O(2) distances. The last two corrrespond to the edges of the octahedra formed by the six oxygen atoms which surround each Cu atom. One

reason for the inclusion of these orbitals and interactions with respect to other works in which different types of instabilities were studied[12,13,15,16], is that these instabilities depend critically on the degree of nesting. This in turn is not only affected by a dispersion along the z component of the wave vector[12], which is expected to be small, but also by the hopping of the O(2) $2p_x$, $2p_y$ orbitals between them and with the Cu $3z^2-r^2$ orbitals, in the manner described in section 3.

In addition, if the hopping integral between Cu x^2-y^2 and O(2) 2p orbitals directed along the Cu-O(2) bond is according to band structure calculations[2-6], the most important one, the Cu $3z^2-r^2$ orbitals cannot be neglected since the corresponding hopping integral is only $\sqrt{3}$ times smaller in the two center approximation[29]. As we show in section 3 only in the case of very strong U or unexpectedly large tetragonal crystal field, the Cu $3z^2-r^2$ orbitals can be neglected.

On the other hand, if only nearest neighbors Cu-O(1) and Cu-O(2) hoppings are included and La states are neglected, it can be shown that the orbitals considered in this calculation constitute an invariant subspace under the application of the Hamiltonian. O - O hoppings are small and can be included perturbatively. Thus, if La, M states and hopping between atoms at distances larger than the length of the largest edge of the CuO_6 octahedra can be neglected, our approximations permit an accurate enough description of the bands that cross the Fermi energy.

In the following section we describe the model Hamiltonian

and the resulting expressions for different spin and charge susceptibilites in the Hartree-Fock approximation.

In section 3 we present the results for three different values of the energy difference between the Cu e_g orbitals, which in turn yield three different shapes of the Fermi surface with different degree of nesting.

Section 4 contains the conclusions.

2.- Model and Relevant Equations

Because of our neglect of La and M states and the hopping integrals between atoms lying at a distance greater than the O(1)-O(2) shortest distance (3.06Å[22,10]), the different layers which contain neighbouring Cu O_6 octahedra are decoupled and the model is two-dimensional. Since the band structure calculations suggest that the La states are far away from the Fermi level[2-6], the most important of the neglected hopping integrals is probably that between $2p_z$ orbitals of O(1) atoms of different $La_{2-x}M_xCuO_4$ layers, which are about 3.2Å apart. We estimate this energy in 0.1 eV from published data for the f.c.c. oxides of transition metals[30] and assuming a $1/r^2$ distance dependence[31].

With the approximations made, the Hamiltonian describes a layer of thickness ~4.8Å which contains a plane of Cu atoms with its nearest O(2) atoms and the O(1) atoms lying immediately above and below this plane. The symmetry group of the layer in the tetragonal phase is the symmorphic group D_{4h}^1. The Hamiltonian can be written in the form:

$$H = \sum_{id\sigma} \epsilon^{di\sigma}_{Cu}\, d^{+}_{i\sigma} + \sum_{j\sigma} \epsilon^{j}_{o}\, p^{+}_{j\sigma} p_{j\sigma}$$

$$+ \sum_{i\gamma d\sigma} \left[t^{\vec{R}_\gamma}_{dp_{i+\gamma}}\, d^{+}_{i\sigma}\, p_{i+\gamma\sigma} + h.c \right]$$

$$+ \sum_{j\delta\sigma} t^{\vec{R}_\delta}_{p_j p_{j+\delta}}\, p^{+}_{j\sigma}\, p_{j+\delta\sigma} \qquad (1)$$

where

$$\epsilon^{di\sigma}_{Cu} = \epsilon^{d}_{Cu} + U \sum_{d'\sigma' \neq d\sigma} \langle d^{'+}_{i\sigma'}\, d^{'}_{i\sigma'} \rangle + \sum_{l \neq i} G_{il}\, q_l \qquad (2)$$

and similarly for ϵ^{j}_{o}. Here d = a or b. $a^{+}_{i\sigma}$ ($b^{+}_{i\sigma}$) creates an electron at site i with spin σ in the 3d orbital of symmetry $3z^2 - r^2$ (x^2-y^2) corresponding to the A_{1g} (B_{1g}) irreducible representation of the group O_{4h}. $p^{+}_{j\sigma}$ creates an electron with spin σ in the 2p orbital of site j which "points" towards its nearest Cu atoms (it has zero angular momentum projection on this direction). The sum over i(j) in (1) runs over all Cu(O) atoms. The first (second) term in (1) represents the energy of the d(p) states. The third (fourth) term describes the hopping between the Cu(O(2)) atoms and its nearest O(1) and O(2) atoms.

Equation (2) gives the Hartree-Fock energies of the d orbitals. The second term represents the effect of the Coulomb and exchange intra-atomic interactions. For simplicity they are described by the same parameter U. The third term, in which q_l is

the total charge on atom 1, represents the effect of interatomic electron-ion and electron-electron interactions on the energy of the d electrons. Since in principle, the value of ϵ^{d}_{Cu} for the paramagnetic undisturbed tetragonal phase can be taken from the band structure calculations[2-6], we are interested in the change of the second member of Eq. (2) under spin or charge density waves. It is reasonable to assume that these waves do not change significantly the value of U. We will also assume that the third term of Eq. (2) remains unchanged. This assumption is based on the works of Harrison[32,33]. He can explain reasonably well several properties of ionic solids using a tight-binding model with atomic term values and no Madelung corrections[32]. He also argues that the effective charges of the atoms vary rapidly with their positions making the effective electrostatic force negligible at the equilibrium distances[33]. The consequences on our results if this statement is not true is discussed at the end of section 3.

We make the same assumption for ϵ^{j}_{o}, neglecting in addition the exchange energy.

The different hopping integrals $t^{R}_{\alpha\beta}$ can be expressed in terms of the two center integrals (pdσ), (ppσ) and (ppπ) at various distances[29]. It is more convenient for us to write the $t^{R}_{\alpha\beta}$ in terms of the absolute value of four of them in the undisturbed structure: t_{bx}(b-O(2)), t_{az} (a - O(1)), t_{xy} (O(2)-O(2)) and t_{xz} (O(1)-O(2)) .

The electron-phonon interaction is derived from the distance

variation of the hopping integrals in a similar way as it was done in refs. 11,15 and 16. We obtain analytical expressions that generalize the ones given in refs. 15 and 16, which took into account only b^{15} and b and O(2) orbitals[16] respectively. The expressions are too long to be reproduced here. We will use them only for the most important phonon modes.

The different quantities of interest are given in terms of the coefficients which in the paramagnetic undisturbed tetragonal structure and for each two dimensional wave vector k, define the states α of maximum energy E_k^α:

$$\alpha^+_{k\sigma} = A_k\, a^+_{k\sigma} + B_k b^+_{k\sigma} + X_k x^+_{k\sigma} + Y_k y^+_{k\sigma} + \frac{Z_k}{\sqrt{2}}\left(z^+_{1k\sigma} - z^+_{2k\sigma}\right) \qquad (3)$$

Here $a^+_{k\sigma}$, $b^+_{k\sigma}$ are the Fourier transforms of the respective $d^+_{i\sigma}$ operators and similarly $x^+_{k\sigma}$, $y^+_{k\sigma}$ ($z^+_{1k\sigma}$, $z^+_{2k\sigma}$) refer to Bloch states of the respective O(2) (O(1)) 2p orbitals. The coefficients and E_k^α are given by the solution of a 5x5 matrix equation.

The spin susceptibility can be obtained applying second order perturbation theory to the paramagnetic state. The change in free energy of the Hartree-Fock Hamiltonian (1) and (2) under a spin density wave of wave vector q and vanishing magnitude is given by

$$\Delta F = \langle s_z(q)\rangle^2 U\,(1-U\chi(q)) \qquad (4)$$

where $s_z(q)$ is the Fourier transform of the total spin of the d electrons at a given site and:

$$\chi(q) = - \sum_{k} |A_k \overline{A_{k+q}} + B_k \overline{B_{k+q}}|^2 \frac{f(E^{\alpha}_{k+q}) - f(E^{\alpha}_{k})}{E^{\alpha}_{k+q} - E^{\alpha}_{k}} \qquad (5)$$

where $f(\in)$ is the Fermi function.

Similarly, when a normal mode "r" with wave vector q of the system is excited to an amplitude "u_{rq}" in the adiabatic approximation, we have for $u_{rq} \to 0$:

$$\Delta F = \frac{1}{2} (K^{r}_{o}(q) - K^{r}_{e}(q)) u^{2}_{rq} \qquad (6)$$

where $K^{r}_{o}(q)$ is given by the frequency of the mode in the absence of electron-phonon interaction and we can write:

$$K^{r}_{el}(q) = -4 \sum_{k} |C^{r}_{k,q}|^2 \frac{f(E^{\alpha}_{k+q}) - f(E^{\alpha}_{k})}{E^{\alpha}_{k+q} - E^{\alpha}_{k}} \qquad (7)$$

The denominators in Eqs. (5) and (7) show that in the presence of near nesting of the Fermi surface, instabilities are more likely to occur for wave vectors q near the nesting wave vector, which in turn is near the symmetry point M of the square Brillouin zone ($Q=(\pi/a, \pi/a)$). This fact was already noted in band structure calculations[2,3,6] and previous tight binding analysis[11-13,15,16]. Then we will restrict our numerical analysis to $q = Q$. The role of the van Hove singularities on the instabilities is also important[4,15] and will be discussed later.

We will restrict our numerical analysis of phonon instabilites to atom displacements in the Cu-O(2) plane,

neglecting any coupling with other modes. This allows us to obtain the normal modes for q=Q without an explicit knowledge of the dynamical matrix, using group theory. The modes corresponding to each irreducible representation at the point M are represented in Fig. 1. They include the already discussed breathing mode[2,11,16,34] (M_1), dimerization mode[15] (M_5^-) and quadrupolar mode[2,16] (M_3). These modes that involve changes in the Cu-O(2) distances are expected to have large unrenormalized frequencies. Then they could satisfy the condition $\omega_{rq} > 2\pi T_c$ for the phonons to be able to give rise to the superconducting transition at a temperature T_c. Among the neglected modes, that in which any two O(1) atoms vibrate in phase towards their nearest Cu atom can have also a large frequency. However, we believe that this frequency is considerably smaller than that of the breathing mode due to the rapid decrease of the Cu-O interaction with distance[33]. These two modes mix at M through the much weaker O(1)-O(2) interactions.

From our electron-phonon calculations we obtain the quantities entering Eq. (7) for the phonon modes represented in Fig. 1. Calling $\tilde{k}_{x_i} = k_{x_i} a/2$ where a is the lattice parameter the result can be written as follows:

$$C_{kQ}^{M_1 (M_3)} = \frac{\sqrt{2}\, t_{bz}}{\lambda_{bz}} \left\{ \frac{}{\overline{B_{k+Q}}} \left[(\pm)\, X_k \sin \tilde{k}_x - Y_k \sin \tilde{k}_y \right] + \right.$$

$$\left. + \frac{\overline{A_{k+Q}}}{\sqrt{3}} \left[(\pm)\, X_k \sin \tilde{k}_x + Y_k \sin \tilde{k}_y \right] \right\} +$$

$$+\frac{2it_{xy}}{\lambda_{xy}}\left\{X_k\,\overline{Y_{k+Q}}\,\sin\tilde{k}_x\cos\tilde{k}_y\,(\pm)\,\overline{X_{k+Q}}\,Y_k\cos\tilde{k}_x\sin\tilde{k}_y\right\}-$$

$$-\frac{2\cos\theta t_{xz}}{\lambda_{xz}}\,\overline{Z_{k+Q}}\left\{(\pm)X_k\sin\tilde{k}_x+Y_k\sin\tilde{k}_y\right\} \qquad (8)$$

$$C_{kQ}^{M_4}=\frac{2t_{xy}}{\lambda_{xy}}\left[X_k\overline{Y_{k+Q}}\cos\tilde{k}_x\sin\tilde{k}_y+\overline{X_{k+Q}}\,Y_k\sin\tilde{k}_x\cos\tilde{k}_y\right] \qquad (9)$$

$$C_{kQ}^{M_5'}=\frac{2t_{bz}}{\lambda_{bz}}\,X_k\cos\tilde{k}_x\left[\overline{B_{k+Q}}+\frac{\overline{A_{k+Q}}}{\sqrt{3}}\right] \qquad (10)$$

θ is the Cu - O(1) - O(2) angle and the quantities $1/\lambda_{\gamma\delta}$ are minus the logarithmic derivative of the two center hopping integrals $t_{\gamma\delta}$ with respect to the distance between the atoms.

With the approximations made, the mode M_2 of fig. 1 and the tilting of the CuO_6 octahedra that is present in the low temperature orthorrombic phase[10,22], do not couple with the electrons in linear order in the displacements, because they leave all the distances of relevance in Hamiltonian (1) unchanged. Instead, the orthorrombic distortion of the oxygen ions with symmetry M_4 shown in Fig. 1, which is also present in the low temperature orthorrombic phase[22], does couple with the electrons through the O(2) - O(2) hopping integrals.

3.- Numerical results

The parameters used in the calculations of the Fermi surface,

$\chi(Q)$ and $K^r_{el}(Q)$ are listed in table 1. The two most important parameters are the difference in energy between the Cu b and the O(2) 2p orbitals in paramagnetic undistorted tetragonal $La_2Cu\ O_4$, and the hopping between them. We took these parameters from the splitting of the A and B bands at the Γ point and the value of $(pd\sigma)$ given in ref.2. They correspond to the two first entries of table 1. Since we found that the results are rather insensitive to the energy of the O(1) orbitals, we took the same energy for all the O orbitals. The energy splitting Δ between the b and a Cu orbitals depends on the crystal field, Coulomb and exchange energies. We made the calculations for three different values of this parameter corresponding to different shapes of the Fermi surface (see Fig.2).

The hopping between Cu a and O(1) 2p orbitals (t_{az}) was taken from the same value of $(pd\sigma)$ assuming a $r^{-7/2}$ distance dependence[31] of this quantity. The O(2)-O(2) and O(1)-O(2) hoppings were deduced assuming a r^{-2} distance dependence[31], from the work of Mattheiss on the band structure of 3d transition-metal monoxides with the rocksalt structure[30]. Since CuO is not in the series we took the values of $(pp\sigma)$ and $(pp\pi)$ of NiO. The dispersion of these values along the series is small. An idea of the error of these estimations is given by the fact that from the value of $(pd\sigma)$ for NiO and a $r^{-7/2}$ dependence one obtains a value of t_{bx} 7% smaller than the one obtained directly from the band structure of La_2CuO_4[2]. Another encouraging fact is that the difference in the width of the bonding and antibonding bands A and B of ref. 2 agrees very well with our result $\sim 4t_{xy}$.

For $1/\lambda_{bx}$ we took the value of the relative variation of t_{bx} with distance quoted in ref. 11. From the $r^{-7/2}$ distance dependence of (pdσ) one would obtain a result 13% larger for the same value. We deduced λ_{xy} and λ_{xz} from the assumed r^{-2} distance dependence of the p-p hopping integrals, since specific values for $La_2Cu\ O_4$ are not available. The good agreement with the distance dependences of ref. 31 for the more important parameter λ_{bx}, suggests that the approximation is reasonable for the mode M_4 and accurate enough for the other modes (see Eqs. (8)-(10)).

For the parameters of table 1, the coefficients of Eq. 3 describing the states near the Fermi energy, can be obtained analytically with enough accuracy for our purposes, making the following four steps approximation:

1) Considering only Cu b orbitals, O(2) 2p orbitals and the hopping between them ,obtaining the antibonding states.
2) Correcting the energy of these states including the O(2)-O(2) hopping in first order perturbation theory.
3) Obtaining the antibonding states from the hybridization between Cu a and O(1) 2p orbitals.
4) Mixing both antibonding states through Cu a - O(2) and O(1)-O(2) hopping.

We have followed this procedure in all the calculations, since it speeds up the two-dimensional numerical integrations involved in Eqs. (5) and (7) to (10).

The first step alone, as noted by Mattheiss[2], is enough to give a rather good description of the bands near the Fermi energy and to explain the superconductivity around 40K within

conventional electron-phonon theory[11,16]. Nevertheless, as we show below, the degree of nesting of the Fermi surface and the predictions for different instabilities as well as phonon softening are affected significantly by the other interactions.

In Fig. 2 we show the resulting Fermi surface for tetragonal undistorted $La_2Cu\ O_4$ in the paramagnetic phase for different (positive) values of the difference in energy between the Cu b and a orbitals. A small part of this energy difference could be ascribed to the tetragonal crystal field. On the other hand, since the a orbitals have a greater occupation due to the smaller hybridization with the O orbitals, the intra-atomic correlations, pushing up the unoccupied levels, give rise to an energy difference in the eV order of magnitude. For example, for $\Delta = \epsilon^b_{Cu} - \epsilon^a_{Cu} = 2.90$ eV (corresponding to the full lines in the figures) we obtain a Cu valence of 1.71. Since most of the d holes are in the b orbitals one obtains from Eq. (2) that this energy difference can be explained if U ~ 8 eV. (In fact, the paramagnetic phase is not stable for this value of U according to our results).

In the range of Δ studied, the result for the Cu valence was between 1.71 and 1.72, corresponding to ~9.3 d electrons. This is the value expected for Cu O and it should be very similar in La_2CuO_4 according to spectroscopic data[27-28].

For very large Δ, the Cu a states can be neglected and the Fermi surface is well described by the antibonding states arising from the hybridization between b and O(2) orbitals. As is already known[2,13-16] the Fermi surface for the stoichiometric compound is

a square if the O(2)-O(2) hopping is neglected. This effect pushes the antibonding states upwards in energy except at the Δ lines ($k_x = 0$ or $k_y = 0$), where the x_k and y_k states do not mix on symmetry grounds. The Fermi level should move to higher energies to keep the number of particles constant. Then the Fermi surface takes the form of the dotted curve of Fig. 2 and the van Hove singularities lying at the X points ($(0,\pi/a)$ and equivalent) stay below the Fermi energy in the stoichiometric compound.

Instead, the effect of the a orbitals is opposite, since the a_k and b_k states belong to the same (different) irreducible representations at the $\Delta(\Sigma)$ line. When $\epsilon^b_{Cu} = \epsilon^a_{Cu}$, this effect dominates because of the larger magnitude (see table 1) of the a -O(2) hopping integral($t_{bx}/\sqrt{3}$) with respect to the O(2)-O(2) one(t_{xy}). The Fermi surface for this case is represented by the dashed line of Fig. 2 and the van Hove singularities lie above the Fermi energy.

The full line in Fig. 2 represents the situation when both effects practically cancel each other.

The density of states per spin corresponding to the three situations is plotted in Fig. 3 as a function of the occupation "n" of the relevant states α .n = 1 corresponds to the stoichiometric compound La_2CuO_4, while in a rigid band picture[5], substitution of La by Sr or Ba reduces n and oxygen deficiency increases n, neglecting scattering with the defects and changes in the parameters. The shape of the three curves is very similar and is dominated by the van Hove logarithmic singularities. However it is important to note that if one moves only 0.016 from the

critical occupation n_x for which the Fermi surface contains the singular X points, the total density of states per Cu atom falls below 2 states per eV in all cases. Then, according to our results, the degree of three dimensionality should be too low and the homogeneity of the sample too high for an explanation of the superconductivity in terms of a divergent density of states[14] to be plausible.

We have calculated $\chi(Q)$ and $K^r_{el}(Q)$ for the same values of Δ and zero temperatures, evaluating numerically the double integrals in k space of Eq. (5) and (7). The result for the antiferromagnetic susceptibility is shown in Fig. 4. For $\Delta = 0$ or very large this function shows the same singularity as the density of states. In the case of perfect nesting ($\Delta = 2.90$ eV), $\chi(Q)$ as a function of the Fermi energy ϵ_F diverges as $\ln^2|\epsilon_F - E^\alpha_X|$ where E^α_X is the energy of the α states at the X points. In the absence of perfect nesting a change in slope of the curves takes place when the Fermi level crosses the points $(\pm\pi/2a, \pm\pi/2a)$. We will denote by n_c the occupation for which these points belong to the Fermi surface. In this situation the vector Q connects two parallel portions of the Fermi surface. The slope at n_c+0 (n_c-0) diverges as $|n-n_c|^{-1/2}$ if $n_c>1$ $(n_c<1)$.

The antiferromagnetic susceptibility decreases rapidly outside the range lying between n_c and n_x, and inside this range it increases with the degree of nesting until both occupations coincide for perfect nesting.

An important conclusion to be drawn from Fig. 4 and Eq. (4) is that for U > 3 eV the system is unstable against

antiferromagnetism for all values of Δ and n in the range of interest. The Coulomb intra-atomic interaction observed in spectroscopic measurements[24] is of order of 6 eV, but the exchange interaction, which is the relevant parameter for the magnetic instabilities is in general smaller. On the other hand, a value of 0.2 eV would result in $\Delta \sim 0.7$ eV from Eq. (2) in the absence of crystal field, and in a magnetic instability that peaks at $n \sim 1.1$ (corresponding to $La_2Cu\ O_{4-y}$ with $y \sim 0.05$) and that disappears for some value of n that is difficult to determine due to the small slope of $\chi(Q)$ near $n = 1$ for small Δ, but in the range $0.85 < n < 1.1$. This agrees qualitatively with the behavior observed in $La_2Cu\ O_{4-y}$[19,20] and $La_{2-x}Sr_xO_4$[21].

The strength of the coupling of the electrons with the different modes depicted in Fig. 1, can be infered from Fig. 5 and Eqs. (6) and (7). K_{el} for the breathing mode M_1 shows an n dependence very similar to that of $\chi(Q)$. This is an indication that for both quantities, the n dependence is determined mainly by the shape of the Fermi surface through the last factor of Eqs. (5) and (7), while the matrix elements connecting the states k and k+Q are rather independent of k at the Fermi surface. The latter fact for the breathing mode was already put in evidence in ref. 16, where the electron-phonon interaction considering only the most important orbitals (b, x and y) was calculated and displayed. However, it is important to include also the a and z orbitals since they are responsible for the three different behaviors shown in each figure.

Contrary to what happens with the M_1 mode, the above

mentioned matrix elements (the C_{kQ} of Eq. (7)) for the M_3 (M_4, M_5') mode(s) vanish on the $\Sigma(\Delta)$ line because of the presence of the corresponding glide planes of symmetry that are conserved by these modes. As a consequence, in the absence of perfect nesting K_{el} is not singular at the occupation $n_c(n_x)$. For the same reason, among the modes considered, only a frozen-in breathing mode (M_1) can open a gap at the Fermi surface if the degree of nesting is sufficiently high.

The fact that the $C_{k,Q}$ should vanish along certain lines for the M_3 and M_5' modes implies a lower sum in Eq. (7) than the corresponding one for the M_1 mode. For the M_4 mode, K_{el} is even smaller because it does not depend on the Cu-O hopping integrals, but on the much smaller O(2)-O(2) ones. The curves for M_4 and M_5' show a peak at n_c and do not diverge for any occupation in the absence of perfect nesting.

When one considers phonons with wave vectors slightly different from Q, the divergences at n_x disappear. The occupation n_c split in two if q is along the Σ direction, otherwise the singularities in the slope also disappear.

In order to be able to discuss the stability of the system against one of the studied phonon modes, we need information about the force constant K_o for this mode in the absence of electron-phonon coupling (see Eq. (6)). An estimation of these constants can be obtained from the phonon spectrum of La_2NiO_4 [35]. This system should contain one electron less in the band structure and then, the softening of the phonons with wave vector Q is expected to be much weaker. Nevertheless, there is evidence of

some softening of several modes at q = Q, particularly the breathing mode. In order to estimate the unrenormalized frequency for this and the M_3 modes we have calculated the dispersion curves of the planar phonons along the line Σ using a simple model with only the Cu-O(2) force constant, which is determined fitting the highest frequency at the Γ point, where the phonon softening seems to be negligible. In this way we obtain a frequency ν = 17.6 THz corresponding to K_o = 20.2 eV/Å^2. From this value, Eq. (6), Fig. 5 and since frozen-in breathing or quadrupolar modes have not been observed[23], we conclude that, as in the case of the antiferromagnetic susceptibility, agreement with experiment is obtained only for small values of Δ. The tiny region of occupations for which K_{el}>20eV/Å^2 for Δ = 0 disappears when 3-dimensional interactions are included. In ref. 23 high frequencies were not investigated. Since the covalent character of the O - transition metal bond increases when going to the right in the periodic table, one expects larger frequencies of the M_1, M_3 and M_5' modes in the Cu compound. First principles calculations for La_2CuO_4[34,36] give a breathing mode frequency almost two times larger as our estimate. If the difference between the bare phonon frequencies of La_2NiO_4 and La_2CuO_4 is really so high, our results restrict the possibility of a frozen in breathing mode in the latter, to almost perfect nesting and n very near to 1. We should mention that according to ref. 34 the calculated potential well is highly anharmonic and with a minimum for |u|~0.02Å. Shell model calculations[37] agree better with the estimate based on the data for La_2NiO_4[35].

Since from ref. 35, K_o for the M_1 and M_3 modes are very similar, but K_{el} is much smaller for the latter (see Fig. 5), an instability against a frozen in quadrupolar mode is ruled out.

Concerning the orthorrombic distortion of the O atoms (M_4 mode of Fig. 1), the electron phonon interaction seems to be too small to produce an instability of this type. From the results shown in Fig. 5, the bare frequency would have to be smaller than ~0.8THz for this instability to occur in the absence of perfect nesting, while the lowest frequency measured in ref. 35 at $q = Q$ is ~ 1.5THz.

With respect to the M_5' mode, of fig. 1, the curves for symmetry Σ_1 and Σ_3 represented in Fig. 1 of ref. 34, that vanish at Γ and become degenerate at the zone boundary, suggest a bare frequency of ~4THz for the Cu dimerization mode. This rather low frequency implies $K_o \sim 4.3$ eV/Å^2. From Eq. (6) and Fig. 5 we see that according to this estimation the system is unstable against the dimerization mode predicted by Barisiç et al[15] in a wide range of values of Δ and n. Nevertheless, since K_o depends on the square of the bare frequency, if the latter for La_2CuO_4 is larger than 5.5 THz for example, the instability disappears if $\Delta = 0$. In any case this instability should compete with the antiferromagnetic one. Note that the first peaks at n_c while the later does it at n_x. This fact suggests again low values of Δ when comparison with experiments is made (for Δ=0, n_x=1.136, n_c=0.837): the largest interaction of the electrons with the dimerization mode is attained for a value of n lower than 1, while magnetic instabilities that can open a gap in the electronic

structure are favoured for n larger than 1. Let us note also that the interaction of the electrons with the breathing mode for $\Delta=0$ is peaked at both n_c and n_x. Though the interaction is probably not enough to result in an instability, it could favour the superconducting behavior at both occupations. If the exchange interaction has such a strength that an antiferromagnetic instability occurs at n_x but not at n_c, the most favourable situation for superconductivity is expected for a compound with composition $La_{2-x}M_xCuO_4$ with $x = 1-n_c$.

To estimate the effects of the last term of Eq. (2) that we neglected, we have repeated some of the phonon calculations including all Coulomb interactions at distances equal or lower than the smallest O(1)-O(2) distance and we have assumed that the charges on the atoms do not change under any displacement. Only the M_1 and M_5' modes are affected by these interactions. For small values of these, K_{el} increases for M_1 and decreases for M_5'. When unscreened Coulomb interactions between point charges are assumed, both K_{el} increase by more than an order of magnitude. In this case, when the arguments of Harrison explained in section 2 do not apply, or for large values of U, the Hartree-Fock theory is invalid and many-body effects should be included from the beginning.

4.- Conclusions

We have considered a tight-binding Hamiltonian that reproduces the essential features of the band structure of paramagnetic tetragonal La_2CuO_4 around the Fermi energy. We have

included O(2), O(1) 2p and Cu 3d orbitals with symmetry x^2-y^2 and $3z^2-r^2$, as well as interactions between them in the Hartree-Fock approximation. The $3z^2-r^2$ orbitals and the O(2)-O(2) hopping integrals modify the dispersion relation around the Fermi energy in quantities of the order of 0.1 eV affecting critically the degree of nesting and with it the spin and charge susceptibilities. The degree of nesting of the Fermi surface is controled by the difference of energy between both Cu orbitals Δ and the number of electrons in the last occupied band n. n = 1 corresponds to stoichiometric La_2CuO_4 while in a rigid band picture n < 1 (n > 1) corresponds to partial substitution of La by Sr or Ba (oxygen deficiency). Δ increases with the Cu intra-atomic Coulomb interaction.

For an intra-atomic Cu 3d exchange interaction U greater than ~3 eV, the system is unstable against antiferromagnetism in all the range of interest of Δ and n. Agreement with the magnetic measurements[19-21] is obtained for $\Delta \lesssim 1$ eV (which implies that the van Hove singularities lie above the Fermi energy) and U ~ 2 eV. For these rather small values of Δ, assuming that the interatomic Coulomb forces (not necessary energies) are negligible and taking phonon frequencies from La_2NiO_4 data[35], only the Cu dimerization (M_5') leads to a lattice instability among the planar phonon modes at the zone boundary, represented in Fig. 1. A 40% larger bare phonon frequency or small interatomic Coulomb repulsions stabilize the system under this mode too. The strength of the electron-phonon interaction has a maximum for n<1. The peculiarities of the n dependence for each phonon mode can be

understood using symmetry arguments. From these, one sees also that only the M_1(breathing) mode (as the antiferromagnetic spin density wave) can open a gap at the Fermi surface.

We believe that for the parameters needed to explain a magnetic instability occuring only for some $n > 1$ ($\Delta < 1$ eV, $U \sim 2$ eV), a quantitative calculation of the superconducting transition temperature would give for the maximum possible value, a similar result as previous calculations[11] or estimates[16] based on a high electron-breathing mode coupling, in which only the most important orbitals (Cu x^2-y^2, O(2) 2p) were near the Fermi energy. The main difference lies in the conditions for which the maximum T_c is obtained. In the above mentioned works the largest electron-phonon interaction was obtained for $n \sim 1$ and the role of divalent metal substitution was to close the gap originated by a frozen-in breathing mode, while in the present picture the doping inhibits the spin density wave and at the same time increases the interaction of the electrons with certain high-frequency modes (M_1 and M_5'). The Cu dimerization mode may be frozen, but it does not open a gap at the Fermi surface and can coexist with the superconductivity[17,18].

If contrary to our assumptions, the description of the interatomic Coulomb forces in terms of unscreened constant point charges is appropriate, the coupling of the electrons with the breathing and Cu dimerization modes is so high that polaronic effects[38] should be taken into account from the beginning.

If the value of the exchange parameter U is as large as the Coulomb interaction observed in spectroscopic measurements[24],

calculations of the antiferromagnetic band structure would be desirable.

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Table 1

$\epsilon^{b}_{Cu} - \epsilon_{o}$	3.50 eV
t_{bx}	1.60 eV
t_{az}	0.77 eV
t_{xy}	0.27 eV
t_{xz}	0.16 eV
λ_{bx}	0.62 Å
λ_{xy}	1.34 Å
λ_{xz}	1.54 Å

Parameters used in the numerical calculations. All of them correspond to the tetragonal undistorted paramagnetic structure. The first is the difference in energy of the Cu x^2-y^2 orbitals with respect to the O(2) orbitals. The next four correspond to the magnitude of x^2-y^2 - O(2), $3z^2-r^2$-O(1), O(2)-O(2) and O(1)-O(2) hopping integrals respectively. The last three give the distance dependence of the corresponding hopping integrals.

Figure Captions

1.- Phonon modes lying in the Cu-O(2) plane for wave vector $Q = (\pi/a, \pi/a)$, classified according to their symmetry.,

2.- Fermi surface of stoichiometric paramagnetic tetragonal La_2CuO_4 for different values of $\Delta = \epsilon^b_{Cu} - \epsilon^a_{Cu}$. Dotted line $\Delta \to +\infty$. Full line Δ = 2.90 eV. Dashed line Δ = 0. The other parameters are listed in Table 1.

3.- Density of states per spin and Cu atom at the Fermi energy as a function of the electronic occupation for the same values of Δ as in Fig. 2.

4.- Antiferromagnetic susceptibility as a function of the electronic occupation for the same values of Δ as in Fig. 2.

5.- K_{el} defined by Eq. (6) as a function of the electronic occupation , for the different modes of Fig. 1 and the same values of Δ as in Fig. 2.

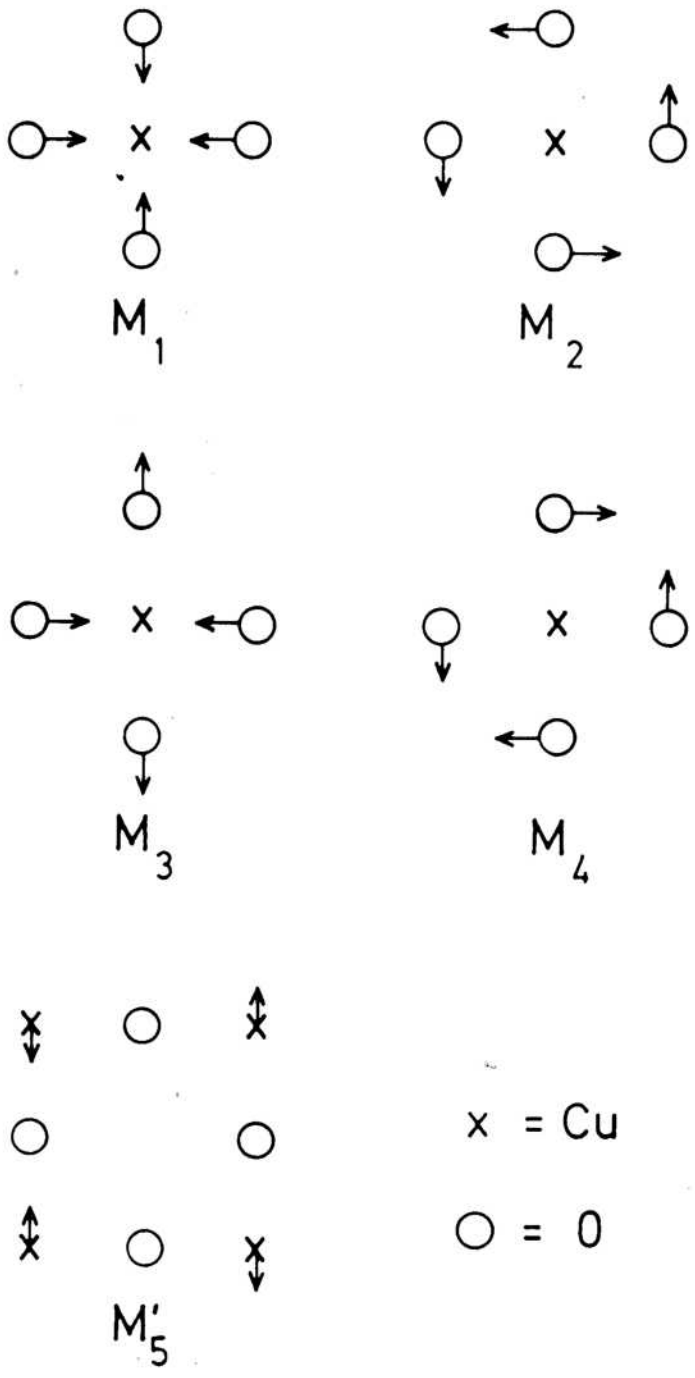

Fig. 1

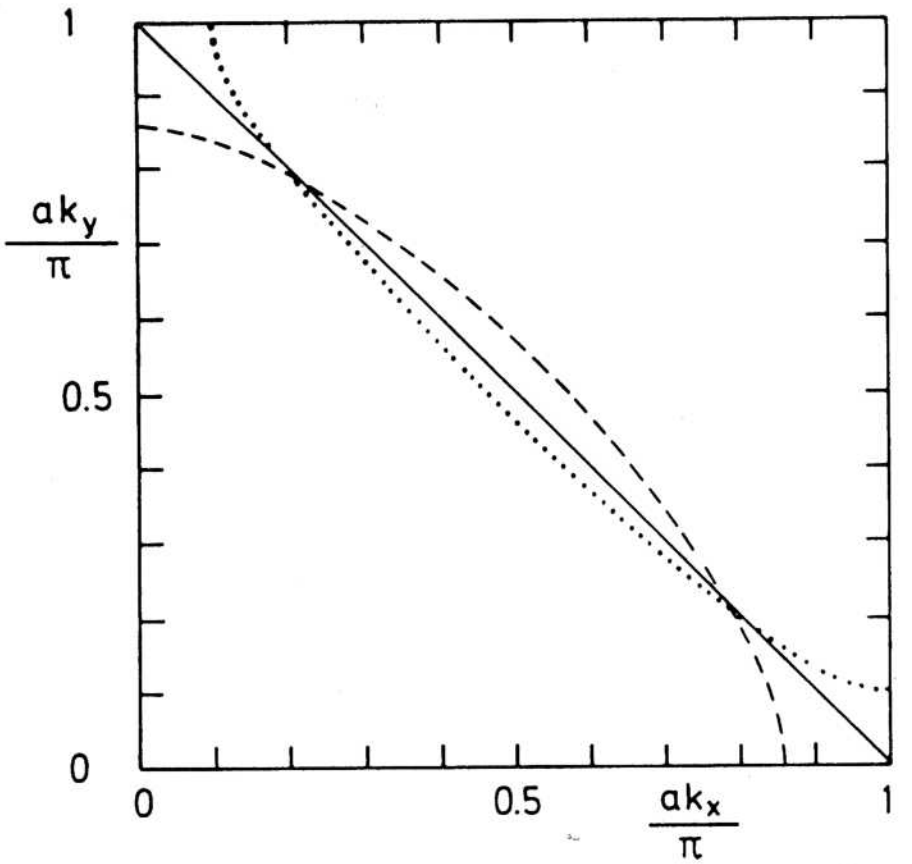

Fig. 2

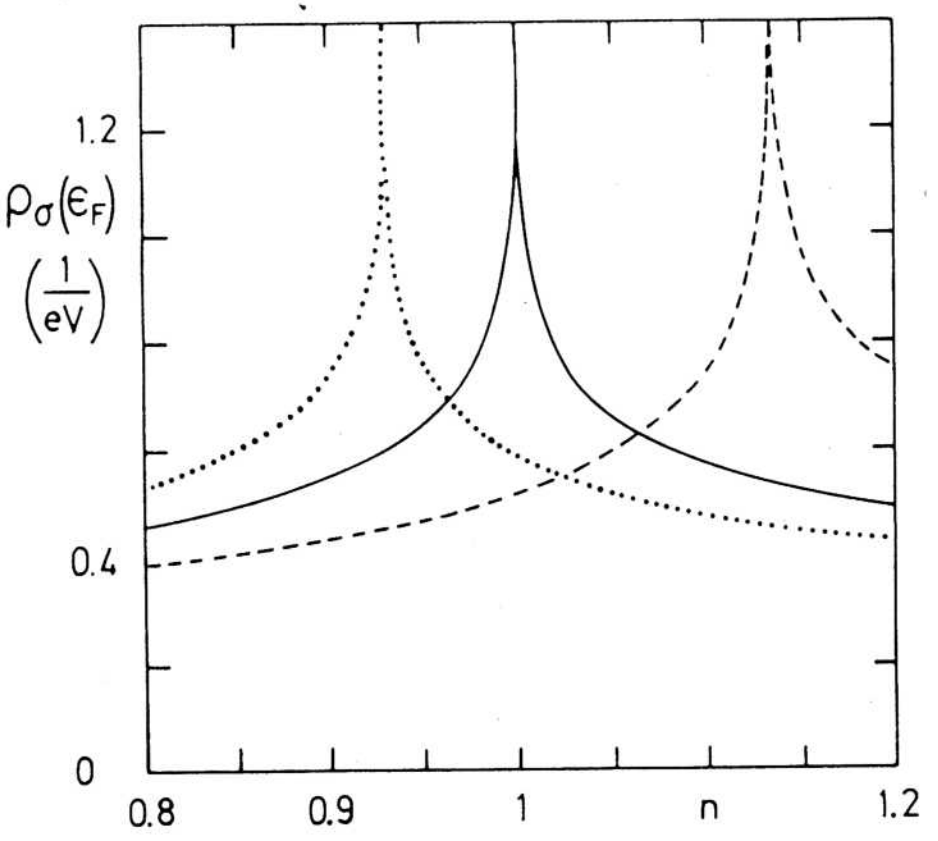

Fig. 3

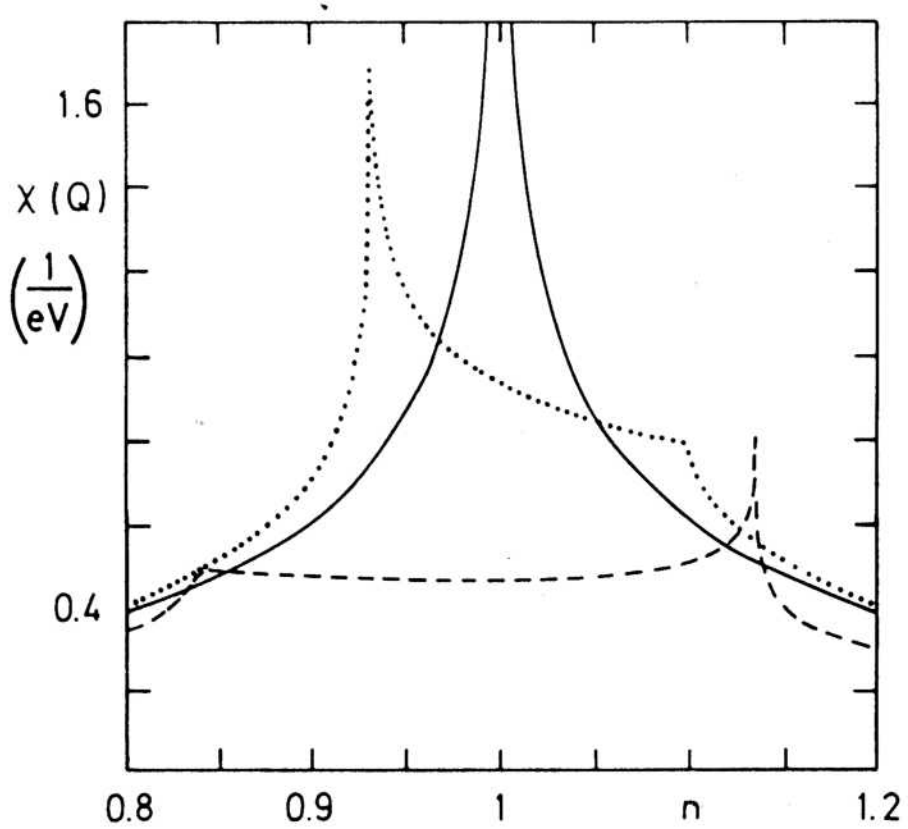

Fig. 4

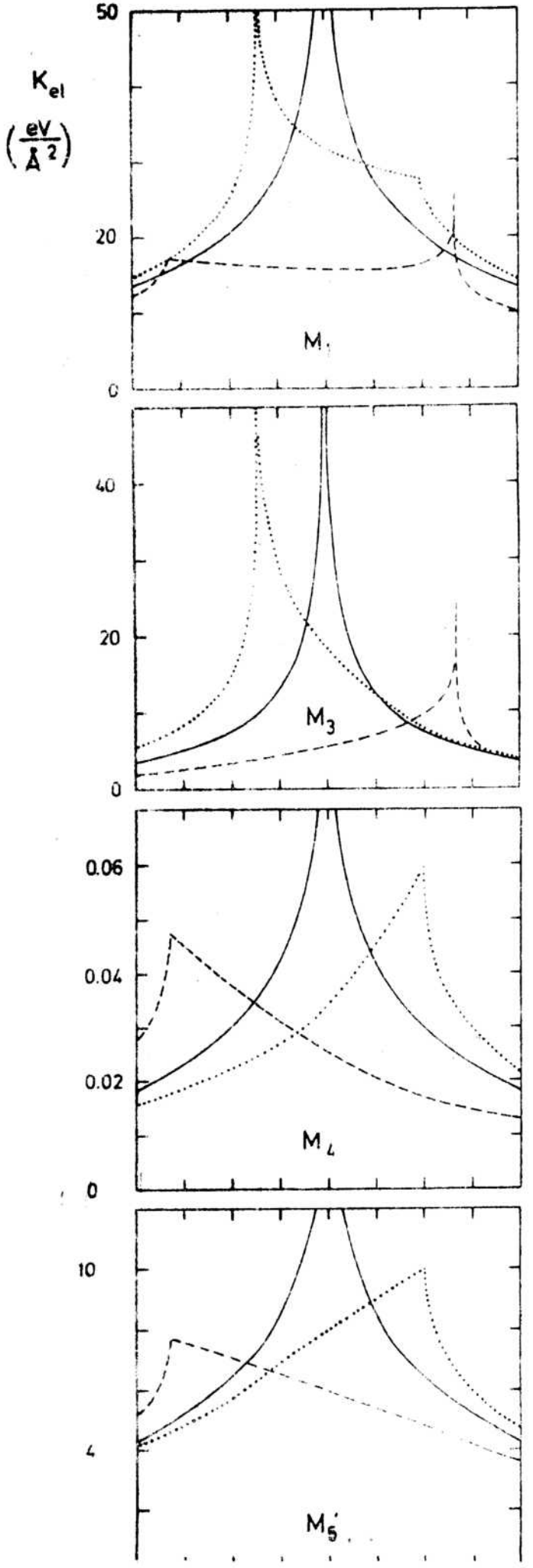
K_{el}
$\left(\frac{eV}{Å^2}\right)$
50
20
0
M_1
40
20
0
M_3
0.06
0.04
0.02
0
M_4
10
4
M_5'

Fig. 5

S.C. DE BARILOCHE, 19 MAYO 1988

SEÑOR DIRECTOR DEL CENTRO ATOMICO BARILOCHE:

De acuerdo con las normas establecidas para la publicación de trabajos (BAP 96/78), elevo para su consideración el trabajo titulado **"Electronically driven instabilities of $La_{2-x}M_xCuO_4$."**

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B.

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BUENOS AIRES, 29 JUN 1988

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