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# ELECTRONIC STRUCTURE AND FERMIOLOGY OF HIGH-T<sub>c</sub> SUPERCONDUCTORS

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We briefly discuss some of our recent results in three areas, all related to issues concerning the electronic structure and fermiology of the high- $T_c$ 's. (i) First-principles band theory based computations of the electron-positron momentum density relevant for the interpretation of the positron annihilation (2D-ACAR) experiments; results for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> are discussed. (ii) Another k-resolved spectroscopy where such first-principles comparisons between the computed and measured spectral intensities have been crucially important is the angle-resolved photoemission experiment; we discuss results for the (001)-surface of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> where computations yield considerable insight into the nature and origin of the spectral signal associated with the CuO<sub>2</sub> plane bands. (iii) The study of effects of substitutions and of oxygen-vacancy disorder in the high- $T_c$ 's; here results for the LaSrCuO<sub>4</sub>, and Ba-K-Bi-O and Ba-Pb-Bi-O systems, with focus on the nature of the van Hove singularity in the vicinity of the Fermi energy are presented. PACS numbers: 71.25.-s, 74.20.Mn, 74.25.Jb

#### 1. Introduction

In these lectures we discuss some of our recent work concerning the electronic structure and fermiology of high- $T_c$  superconductors. The specific topics considered are: the interpretation of the positron annihilation two-dimensional angular correlation (2D-ACAR), and of angle-resolved photoemission spectra (ARPES) in Y-123 in terms of the corresponding first-principles computations of the spectral intensities within the conventional band theory framework, and *ab initio* studies of effects of substitutions on the electronic structure of high- $T_c$ 's. Our motivation for considering these topics is as follows.

Concerning positron studies, the crucial importance of model theoretical predictions as a basis for interpreting 2D-ACAR spectra has been evident since the inception of this spectroscopy as a tool for investigating the electronic structure of materials [1, 2]. 2D-ACAR studies of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> started immediately [3-5] after the discovery of this compound because this experiment is ideally suited to answer one of the fundamental questions, namely, whether or not the electron momentum density in the new materials possesses Fermi surface (FS) breaks like the conventional metals. Results in this regard would provide guidance in searching for a suitable theoretical description of the electronic structure, and thus help develop an understanding of the mechanism of superconductivity. A good understanding of the observed 2D-ACAR spectra, including various FS signatures therein, has been possible within the band theory framework, at least in metallic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>; an overview of these results is given in Sec. 2 [6-11].

Turning to angle-resolved photoemission studies, we note that ARPES is playing an important role in connection with the electronic structure of the high- $T_c$ 's; see Refs. [12] and [13] for a discussion of various recent issues. Photoemission however involves complex processes of excitation and transport of the photoemitted electrons followed by transmission through the solid surface; the imprints of the initial bulk states which are of primary interest in many solid state applications can often be masked and/or modified by these processes and by the possible presence of spectral features arising from other effects, such as the surface states and surface resonances, final state effects, the density of states peaks, etc. [14]. It is clear then that first-principles computations of the ARPES intensities within the band theory framework would give insight into the nature and origin of some of the observed spectral features; direct comparisons between theoretical and experimental spectra would also help isolate spectral aspects where the validity of the local density approximation (LDA), implicit in the calculations, is to be questioned. Motivated by these considerations, we have developed the first-principles methodology for obtaining ARPES intensities by generalizing the "one step" photo emission approach [15, 16] so that systems with the complexity of the high- $T_c$ lattices can be treated [17, 18]. Some results concerning the (001)-surface of Y-123 are discussed in Sec. 3.

Finally, concerning substituted compounds, we note that while reliable predictions of the electronic structures of ordered compounds with many atoms per unit cell have been obtained using the LDA, a comparable description of the disordered phases has been lagging, even though wide variations in properties with different substitutions are commonly observed. The band theory of ordered phases is not suited for exploring a variety of phenomena in materials, and it is clear that the first-principles Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) approach, which has already proven successful in simple binary alloys [19–24], needs to be generalized to treat complex systems. It should be noted however that limited progress can often be made via the use of virtual crystal, rigid band, and supercell-type models, and also via the tight-binding CPA framework with parameters chosen to fit the band structures of the end-compounds. Nevertheless, as the extensive experience with binary alloys shows, the simpler tight-binding CPA and rigid band type models cannot be expected to provide a realistic description of the disordered phases; if anything, these simpler models are likely to become generally less reliable as the complexity of the unit cell increases. With this motivation, we have developed and implemented the charge

and spin self-consistent KKR-CPA approach to treat disorder effects in complex materials on a first-principles basis [24-26]. Section 4 considers the simple cubic perovskites, Ba-K-Bi-O and Ba-Pb-Bi-O, and the La<sub>2</sub>CuO<sub>4</sub> with substitutions on the La-sites, as examples of the application of the multi-component KKR-CPA methodology.

Our purpose in this article is to be illustrative rather than exhaustive. The discussion of the few applications of the theory presented as examples is by no means complete, although an effort has been made to cite work where more details can be found; otherwise the reference to literature is meant to be minimal.

#### 2. Positron annihilation (2D-ACAR) studies

A positron annihilation (2D-ACAR) measurement is related to the three-dimensional (3D) electron-positron momentum density relevant for the  $2\gamma$ -annihilation of a positron with the Bloch electron gas in a crystal [1, 2, 27], i.e.

$$\rho_{2\gamma}(p) = \sum_{k,j} f(E_{k,j}) \left| \int \exp(-\mathrm{i}p \cdot r) \psi_{k,j}(r) \phi_+(r) \mathrm{d}r \right|^2, \tag{1}$$

where  $\phi_+(r)$  denotes the e<sup>+</sup> ground state wave function, and  $\psi_{k,j}(r)$  is the electron (e<sup>-</sup>) wave function for crystal momentum k and band index j.  $f(E_{k,j})$  is the Fermi-Dirac distribution function which restricts the summation to the occupied electron states. In writing Eq. (1) we have assumed that the electrons and positrons are independent particles. The effects of electron-positron correlations so neglected have often been incorporated semi-empirically using various schemes, and generally do not affect the shape of  $\rho_{2\gamma}(p)$  drastically (as opposed to the positron lifetime) [28]. In a 2D-ACAR experiment, one essentially measures the 2D-projection of  $\rho_{2\gamma}(p)$ , i.e.,

$$N_{2\gamma}(p_x, p_y) = \int_{-\infty}^{+\infty} dp_z \, \rho_{2\gamma}(p_x, p_y, p_z),$$
(2)

where the axis of the positron camera is taken to be aligned along the z-axis. To proceed further we require a specific choice of the band structure methodology. Our momentum density computations are based on the KKR band structure scheme using non-overlapping muffin-tin potentials to represent the atoms; see Refs. [6] and [27] for details.

We note that a Compton scattering experiment constitutes another probe of the electron momentum density and involves the quantity

$$\rho(p) = \sum_{k,j} f(E_{k,j}) \left| \int \exp(-\mathrm{i}p \cdot r) \psi_{k,j}(r) \mathrm{d}r \right|^2,$$
(3)

which is obtained from Eq. (1) by neglecting the positron wave function. However, the Compton scattering experiment usually measures a one-dimensional projection (much like the older 1D-ACAR studies) of  $\rho(p)$  [29, 30]:

$$J(p_z) = \int \int \mathrm{d}p_x \mathrm{d}p_y \,\rho(p_x, p_y, p_z). \tag{4}$$

In comparing positron annihilation and Compton scattering, note that the interpretation of the positron spectroscopy is complicated by the presence of positron spatial distribution effects, and the positron, being repelled by ionic cores, preferentially samples valence rather than the core electrons. Compton scattering, in contrast, involves all electrons, and thus yields a relatively smaller signal from the valence electrons. We should keep in mind nevertheless that in the 2D-ACAR experiment only a 1D integral is required (Eq. (2)), whereas the Compton spectrum involves a 2D integral in Eq. (4) which will generally make it harder to discern spectral features of  $\rho(p)$  in the observed Compton profiles. On the whole though it would be sensible to view these two spectroscopies as being complementary, and with recent and anticipated improvements in the momentum resolution, it would be most worthwhile to develop Compton scattering as a probe of fermiology of materials.



Fig. 1. A comparison of various sections through the background corrected 2D-ACAR spectrum on an untwinned  $YBa_2Cu_3O_{7-x}$  sample with the corresponding theoretical predictions for the *c*-axis projection. The experimental results are after Ref. [11], theoretical results are after Refs. [6] and [7]. The momentum on the horizontal scale is in units of milliradians (1 mrad = 0.137 a.u.).

We illustrate the application of the 2D-ACAR spectroscopy in connection with the high- $T_c$ 's by considering some of our results for the *c*-projected momentum density in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. Figure 1 compares the computed and experimental 2D-ACAR's for many different sections through the distribution; the experimental data here have been corrected for a nearly isotropic background contribution, see Ref. [11] for details. Lines passing through the  $\Gamma$ -point as well as through symmetry points in higher Brillouin zones are considered. Anisotropies are quite evident by inspecting the spectra, e.g. by comparing the  $\Gamma X$ ,  $\Gamma Y$ , and  $\Gamma S$  cuts. The two sets of curves possess very similar shapes not only for low momenta, but at higher momenta as well, and the overall agreement between theory and experiment in Fig. 1 is remarkably good.



Fig. 2. (a) Theoretical anisotropic momentum distribution defined by taking differences in  $N_{2\gamma}(p_x, p_y)$  along four different pairs of directions (after Ref. [7]). Thin vertical lines mark the positions of various FS features  $r_0$ ,  $s_1$ , etc. discussed in the text. (b) A comparison between the resolution broadened theory curves in (a) with the corresponding experimental difference sections obtained from the data of Fig. 1.

The anisotropies, in the form of differences in the spectra along various pairs of directions, are considered in Fig. 2. In this way, isotropic contributions are subtracted and the FS features are enhanced. We comment on the theoretical results of Fig. 2a first, which clearly displays many "breaks" (e.g.  $r_1$ ,  $r_2$ ,  $s_5$ , etc.) associated with the Fermi surface. Note that the FS breaks in Fig. 2a occur in a distribution which itself possesses substantial underlying structure. As a result, when the theoretical spectra are broadened to include experimental resolution, some FS breaks are more likely to remain distinct compared to others.

Before discussing FS signatures in Fig. 2a, we recall that the band theory predicts the FS of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> to consist of four sheets [6, 31, 32]. For the band structure implicit in our calculations these are: (i) a pair of closely placed S-centered hole sheets which possess the shape of the outer and inner surfaces of a "barrel" (Figs. 3a and 3b), (ii) an electron "ridge" surface running along  $\Gamma X$  (Fig. 3c), and (iii) a "pillbox" hole-sheet around S and hole "butterflies" (Fig. 3d). The FS of Fig. 3 is in reasonable accord with other computations; the pillbox and the butterflies which arise from a heavy mass band that lies close to the Fermi energy are however sensitive to computational details and differ somewhat between various calculations.

Keeping Fig. 3 in mind, the signatures of various FS sheets in Fig. 2a are as follows. The ridge FS gives the rapid variation  $(r_0)$  near p = 0; since the ridge lies along the  $\Gamma X$  direction, in the  $\Gamma S \cdot \Gamma X$  spectrum or other difference spectra involving the  $\Gamma$ -point, the anisotropy is nearly zero for momenta (around p = 0) of



Fig. 3. Intersections of the four Fermi surface sheets in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> with the  $\Gamma XSY$  plane (after Ref. [6]).

the order of the width of the ridge. The first umklapp image of the ridge  $(r_1, r_2)$  is seen clearly around 6.3 mrad as a peak in  $\Gamma Y$ - $\Gamma X$ , and a dip in  $\Gamma S$ - $\Gamma Y$ ; only weak features are seen at this momentum in the  $\Gamma S$ - $\Gamma X$  or XS-YS curves. The second image of the ridge  $(r_3, r_4)$  occurs around 13 mrad. The high momentum end  $r_4$  is generally more clearly visible than the low momentum feature  $r_3$ . The pillbox FS yields relatively prominent features only in the XS-YS spectrum; the four breaks  $s_1, s_2, s_3$ , and  $s_4$  are all associated with the pillbox. Interestingly, the image of the pillbox around 9.5 mrad  $(s_5, s_6)$  only consists of two prominent breaks; this results from the fact that in this momentum region, the pillbox possesses a substantial signature only along the YS and not the XS direction. We note that the butterfly FS gives small features in the anisotropic spectra (not labelled in Fig. 2a). Finally, the Cu-O plane sheets essentially give no discernible signatures in the 2D-ACAR's as a result of the weak coupling of the positron Bloch state with the Cu-O planes. [6-9].

Figure 2b shows that experimental anisotropies are in good accord with theory with regard to both the details of the spectral features, and also the absolute magnitude of the overall undulations. The level of discrepancies seen here is common in even simpler materials in first-principles comparisons between theory and experiment. FS signatures in the experimental spectra can be elucidated with reference to Fig. 2b. We consider the ridge FS first. As noted above, the ridge FS gives three distinct features: (i) rapid variation in anisotropy near p = 0, (ii) an image around 6.3 mrad, and (iii) a second image around 13 mrad. The experimental spectra display all three of these features. The 6.3 mrad image of the ridge  $(r_1, r_2)$  is particularly important in the  $\Gamma Y - \Gamma X$  curve because this feature lies on a relatively gently varying background and remains quite prominent in the theory even after including resolution broadening, and it is crucial that this feature is indeed observed clearly in the experimental data. By contrast, in the  $\Gamma S - \Gamma Y$  curve, the resolution broadening effects would make the 6.3 mrad ridge image difficult to distinguish from the background. The image of the ridge FS near 13 mrad  $(r_3, r_4)$  becomes rather smooth in theory upon resolution broadening; we emphasize however that the experimental data in this momentum range is quite consistent with the theory. Finally, concerning the pillbox, the dip arising from the breaks  $s_5$  and  $s_6$  remains distinct even after resolution effects are included, and in this momentum region, the experimental data indeed clearly display a similar dip in accord with the theory.

#### 3. Angle-resolved photoemission intensities in high- $T_c$ 's

Our angle-resolved photoemission calculations are based on the use of the "one step" formulation [15, 16] in which the photoemission process is treated as a single quantum mechanical event, and artificial distinctions between the processes of excitation, transport, and transmission of the electron through the surface barrier invoked in the earlier "three step" type model are removed [14]. In the one-step approach the intensity of photoemitted electrons of a given energy E and emission direction  $k_{\parallel}$  for incident radiation of frequency  $\omega$  can be written as [16]:

$$I = -\frac{1}{\pi} \mathrm{Im} \langle k_{\parallel} || G_2^+ \Delta G_1^+ \Delta^{\dagger} G_2^- || k_{\parallel} \rangle,$$
(5)

where  $G_2$  and  $G_1$  are one-electron Green's functions at the final state energy  $(E + \hbar \omega)$  and the initial state energy E respectively; the superscripts + (-) on Green's functions indicate forward (backward) propagation, and  $\Delta$  is the photon field operator. Practical photo-intensity computations employ the semi-infinite muffin-tin Hamiltonian where atoms are represented by non-overlapping muffin-tin potentials, and the surface is separated from the vacuum by a step  $V_{\text{inner}}$ , the "inner potential". Following common practice, the self-energy corrections to the potential may be incorporated via a semi-empirical step potential at the surface of the form,  $V_{\text{inner}} = V_{\text{R}} + iV_{\text{I}}$ . The analysis of form (5) proceeds most naturally via the use of multiple-scattering theory and low-energy-electron-diffraction type techniques; see Ref. [33] for details.

In connection with the high- $T_c$ 's, we have developed the methodology and the associated semi-relativistic computer codes capable of handling essentially an arbitrary number of basis atoms in the unit cell [17, 18]. Previous work has been limited to the case of up to two atoms in the layer unit cell [34]. The high- $T_c$ 's however require the treatment of much larger basis sets; for example, in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, the (001)-surface involves 3 atom basis, and the (100)-surface at least 9 basis atoms. Further technical complications arise due to the presence of "buckling" of layers; also, the presence of heavy atoms in most high- $T_c$ 's necessitates the use of at least a semi-relativistic treatment of electronic states.

We have considered the (001)-surface of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> as our first case study; here we give two examples of the sort of insight present first-principles computations can provide into the nature of ARPES spectra of the high- $T_c$ 's.

Figure 4 shows theoretical spectra for emission along the  $\Gamma S$  line for three different terminations of the (001)-surface; for brevity, we do not show the results corresponding to three other unique terminations admitted by the crystal structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The range of emission angles  $0 \le \theta \le 15^{\circ}$  considered here



Fig. 4. Theoretical ARPES spectra from the (001)-surface of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> for three different surface terminations, T1-T3; the two topmost layers are identified in the legend and uniquely specify the termination. The experimental spectra are for unpolarized HeI radiation; the photoelectrons are collected in the same plane at various angles  $\theta$  with respect to the surface normal. The solid and dashed curves give theoretical spectra with and without Fermi cut-off in the computations. The peaks denoted by letters A-Ecorrespond to various bands near the Fermi energy (after Ref. [18]).

encompasses the experimental feature b which is seen clearly in all published spectra [35-39] and the weaker feature b', which have been widely interpreted as the crossing of two closely placed Cu-O plane bands around  $\theta = 13^{\circ}$  and  $\theta = 7^{\circ}$ . We see that various bands near the Fermi energy (denoted by letters A through E) all give features in the spectra of Fig. 4, but the relative intensities differ greatly between various surface terminations (denoted by T1 through T3). For example, the termination T3 (BaO/CuO...) gives prominent structures from bands D and E, while T1, also Ba-terminated, is dominated by bands B and C. Note that all the computed spectra are based on the same underlying band structure; the differences in spectral shapes reflect effects of multiple scattering and matrix elements inherent in the photoemission process.

Figure 5 considers the detailed polarization dependence of the intensity of the  $CuO_2$  plane related peaks near the Fermi energy [18]; these are the peaks b and b' in the experimental spectra and the features denoted by B and C in theoretical spectra of Fig. 4. The results for the BaO/CuO<sub>2</sub> termination (T1) are compared in Fig. 5 with the corresponding measurements and show an excellent accord; the intensity is small for polarization  $A \parallel \Gamma S$ , and large for  $A \perp \Gamma S$  direction. The theoretical signature of CuO<sub>2</sub> bands in Fig. 5 (solid curve) is rather robust in that the results of computations for other terminations (not shown) where the



Fig. 5. The computed intensity of the CuO<sub>2</sub> plane band feature as a function of the azimuthal angle of polarization of the incident light (solid curve); the results are for a fixed value of  $k_{\parallel}$  (along the  $\Gamma S$  direction) as the CuO<sub>2</sub> plane bands cross the Fermi energy and are not sensitive to the precise value of  $k_{\parallel}$ . (Note, the computations of Fig. 4 are for unpolarized radiation, whereas Fig. 5 is based on computed spectra for polarized light.) The experimental results are given by filled circles on which the direction of the polarization vector is shown by double arrows. The normalization between theory and experiment was determined by requiring agreement at the  $A \perp \Gamma S$  point (after Ref. [18]).

plane band peaks could be identified are very similar. Also, theoretically as well as experimentally the CuO<sub>2</sub> plane bands are not excited by the z-component  $A_z$ . We emphasize that the agreement in Fig. 5 does not merely reflect the symmetry properties of the lattice, but provides a test of the character of the underlying LDA based band theory wave functions implicit in the computations. Indeed, similar calculations of the azimuthal dependence of the intensities of other bands such as the CuO chain bands (these have however not so far been identified in the ARPES data) show that plots like those of Fig. 5 possess many different shapes, and even for the same band this signature can in general vary between different terminations.

#### 4. Effects of substitutions in high- $T_c$ 's

As already noted, our treatment of the effects of substitutions on the electronic structure of the high- $T_c$ 's is based on the use of the KKR-CPA approach [19-24]. In these calculations, no free parameters other than the lattice data are involved; this restriction may also be removed, at least in principle, by minimizing the total energy of the system as a function of the interatomic spacings. Concerning our formulation of the multi-component KKR-CPA methodology, we especially note two general points [24-26]. First, we consider full KKR-CPA Green's function, including terms which are real on the real energy axis even though such terms do not contribute to the density of states; our experience is that without the use of full KKR-CPA Green's function, it becomes difficult to reliably carry out and automate spin and charge self-consistency KKR-CPA cycles in the complex energy plane. Second, we have used the spectral representation of KKR-CPA Green's function to implement a tetrahedron-type k-space integration method for disordered alloys. This approach yields orders of magnitude gains in efficiency, and also allows us to treat for the first time the limiting cases of the single-impurity and the ordered compound with the same set of codes, permitting satisfactory intercomparisons between the electronic structures of the parent compound with and without impurities.

We discuss here briefly two examples of multi-component KKR-CPA calculations. Some results for the simple cubic perovskites  $Ba_xK_{1-x}BiO_3$  (BKB) and the  $BaPb_{1-x}Bi_xO_3$  (BPB) which we have investigated extensively [26] are presented in Figs. 6 and 7. Fully charge self-consistent KKR-CPA computations were carried out in  $Ba_xK_{1-x}BiO_3$  and  $BaPb_{1-x}Bi_xO_3$  for 11 compositions x = 0.0, 0.1,...1.0 in each case; x = 0.0 and x = 1.0 represent the case of a single impurity in the host. Figure 6 gives the total KKR-CPA density of states in BKB and BPB



Fig. 6. Charge self-consistent KKR-CPA total densities of states in  $Ba_xK_{1-x}BiO_3$  and  $BaPb_{1-x}Bi_xO_3$ . The Fermi energies  $(E_F)$  are as marked (after Ref. [26]).

for a representative set of compositions. Figure 7 compares the density of states at the Fermi energy  $(E_{\rm F})$  in the alloys with the corresponding predictions of the rigid band model based on the BaBiO<sub>3</sub> density of states. Figures 6 and 7 allow us to delineate the rigid band as well as non-rigid band changes in the spectrum of BaBiO<sub>3</sub> induced by (Ba-K) and (Bi-Pb) substitution.

Figure 6a shows that for energies around the Fermi energy of BaBiO<sub>3</sub>, the shape of the density of states curve is little affected by Ba-K substitution. In



Fig. 7. Total density of states at the Fermi energy for the BaBiO<sub>3</sub>-based rigid band model, and the KKR-CPA results in  $Ba_xK_{1-x}BiO_3$  and  $BaPb_{1-x}Bi_xO_3$  (after Ref. [26]). Fig. 8. The KKR-CPA density of states in the disordered  $La_{1.8}M_{0.2}CuO_4$  (M is Sr, Ba, or Ca) is compared with the corresponding KKR results for  $La_2CuO_4$ .

contrast, the Pb-Bi substitution, rapidly smooths the cusp at  $\approx 0.6$  Ry (Fig. 6b). This effect is related to the fact that the density of states around  $E_{\rm F}$  in BaBiO<sub>3</sub> arises mainly from Bi- and O-sites, which are not influenced substantially when Ba is replaced by K; the Pb- and Bi-site densities on the other hand are quite different in this energy region, and thus lead to considerable changes upon alloying. Interestingly though the total density of states at  $E_{\rm F}$  in both alloys (Fig. 7) is rather close to the predictions of a BaBiO<sub>3</sub>-based rigid band model. However, in view of the preceding observations, the agreement between the rigid band and the KKR-CPA results in Fig. 7 in the case of BPB should be considered fortuitous.

Turning to the energy region of 0.15 to 0.45 Ry, Fig. 6 shows that the shape of the density of states curve is quite similar in BKB as well as BPB for  $0.3 \le E \le 0.45$  Ry in the upper part of the Bi 6s-O 2p complex. For lower energies,  $0.15 \le E \le 0.3$  Ry, we see substantial changes in the spectrum. For example, the largest peak at 0.29 Ry in BaBiO<sub>3</sub> splits and becomes less prominent in BKB; in contrast, this peak is rather unaffected in BPB. The relative weights, positions, and shapes of the density of states peaks at 0.23 Ry and 0.25 Ry in BaBiO<sub>3</sub> are influenced considerably in both BKB and BPB. The preceding changes in the spectra between 0.15 and 0.3 Ry arise not only from changes in the component densities of states associated with the substituted sites, but also from the indirect changes induced on the O- and other sites as a result of alloying.

Figure 8 considers the effects of substitutions on the La-site in  $La_2CuO_4$  [24].

17

We have carried out self-consistent KKR-CPA computations in La<sub>1.8</sub>M<sub>0.2</sub>CuO<sub>4</sub> for the ideal body centered tetragonal lattice assuming random occupation of the La-sites by La and M atoms (M is Sr, Ba, or Ca), together with a corresponding self-consistent KKR calculation of the parent compound La<sub>2</sub>CuO<sub>4</sub>. The total density of states in La<sub>2</sub>CuO<sub>4</sub> and La<sub>1.8</sub>M<sub>0.2</sub>CuO<sub>4</sub> is compared in Fig. 8. Aside from an overall smoothing of the density of states, the main effect is the lowering of the  $E_{\rm F}$ on replacing trivalent La atoms by divalent Ba, Ca, or Sr atoms. In particular, the shape of the density of states curve near  $E_{\rm F}$  is hardly affected by substituting on the La-site, although relatively larger effects are generally present at higher binding energies, especially for La/Ba replacement. These *ab initio* results support the rigid band picture [40] of the electronic structure of La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub>, based on band theory computations on La<sub>2</sub>CuO<sub>4</sub> is insulating, not metallic as predicted by the band theory.

## 5. Conclusions

We have presented an overview of the theoretical methodology in three areas all related to exploring the electronic structure and fermiology of high- $T_c$ 's within the band theory framework. These are: (i) computations of the electron-positron momentum density measured in a 2D-ACAR positron annihilation experiment, (ii) calculations of the spectral intensities measured in angle-resolved photoemission experiments, (iii) first-principles predictions of the effects of substitutions on the electronic states. Illustrative examples of the methodology in each of these areas are given. The good accord between theory and experiment in the case of 2D-ACAR and the ARPES spectra from YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> indicates that aspects of the electronic spectrum of this compound can be described reasonably within the conventional band theory framework, including the states associated with the CuO<sub>2</sub> plane bands. Finally, we have shown that the KKR-CPA approach provides a sophisticated parameter free theory for obtaining insight into the effects of substitutions on the electronic states in complex materials.

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