Electronic structure and properties of quasi-two-dimensional layered superconducting perovskites: $La_{2-x}M_xCuO_4$ (M = Ba, Sr, . . .)

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Results of highly precise all-electron local-density calculations are presented for the quasi-two-dimensional superconductors $La_{2-x}M_xCuO_4$ (M = Ba, Sr, . . .) with $x = 0$ and correlated with a number of observed properties of these materials for varying x. The dominant role of the van Hove saddle-point singularity (SPS) on the density of states (DOS) and the DOS-derived properties (specific heat, magnetic susceptibility, T_c) is emphasized—as is the fact that this SPS represents the classic Lifshitz transition versus x (and/or pressure) with its possible thermodynamic and galvanomagnetic anomalies. Estimates of the enhancement factor λ from a variety of measured specific-heat values and our calculated DOS indicate that these materials may possibly be weak-coupling superconductors. Crude estimates of coherent lengths ($\xi_\parallel$ and $\xi_\perp$) and upper critical fields ($H_{c2\parallel}$ and $H_{c2\perp}$) are presented.

The high-T_c superconductors,[1] $La_{2-x}M_xCuO_4$ (M = divalent metal, Ba, Sr, . . .) continue to grow in experimental and theoretical interest.[2-4] In a previous paper,[5] we presented some first results of the electronic structure and properties of body-centered tetragonal (bct) La_2CuO_4 which showed that the electronic structure and properties are dominated by strong in-plane interactions between the Cu d and O(1) $2p$ electrons. The results of this highly precise all-electron local-density full-potential linearized augmented plane wave[6] (FLAPW) energy-band calculation of the band structure, charge densities, Fermi surface (FS), etc., demonstrated (i) that the material consisted of metallic Cu-O(1) planes separated by insulating (dielectric) La-O(2) planes and (ii) that this two-dimensional (2D) character and alternating metal/insulator planes would have as some of their most important consequences, strongly anisotropic (transport, magnetic, etc.) properties.[5] While measurements to data have been done only on powders, it is clear that synthesis and measurements on single crystals of these materials are an urgent priority and results are expected shortly.

In this paper we present detailed results on the electronic structure, especially density of states of La_2CuO_4, which we correlate with varying composition x of the M = divalent additions and resulting properties. We emphasize that a highly important role is played by a strong 2D van Hove saddle-point singularity (SPS) in the electronic band structure and properties for $x > 0$. This SPS dominates the density of states at and near E_F. As reported elsewhere,[7] it also strongly affects the Fermi surface and the generalized susceptibility $\chi(\mathbf{q})$. It turns out that this material demonstrates vividly the classic case of an SPS first discussed in the work of Lifshitz[8] who showed how a change in the topology of the Fermi surface is accompanied by the appearance of various anomalies in the thermal and electronic properties. Later, Dagens[9] and others have emphasized the occurrence of phonon anomalies near such a FS topological phase transition and possible changes in T_c as well.

The calculated band structure was shown previously[5] along high-symmetry directions in the Brillouin zone. Only flat bands, i.e., almost no dispersion, were found along the c axis, demonstrating that the interactions between the Cu, O(2), and La atoms are quite weak. However, along the basal plane directions there are very strong interactions between the Cu-O(1) atoms leading to large dispersions and a very wide bandwidth (~9 eV). The band structure near E_F has a number of interesting features. What is especially striking is that, in contrast to the complexity of its structure, only a single free-electronlike band crosses E_F and gives rise to a simple Fermi surface (cf. Fig. 1). Since this band originates from the Cu $d_{x^2-y^2}$-O(1) $p_\parallel$ orbitals confined within the Cu-O(1) layer, it exhibits clearly all the characteristics of a 2D electron system. Particularly striking in Fig. 1 is the occurrence of a van Hove saddle-point singularity (note arrow in the figure) near the G_1, N, and G_4 points in the Brillouin zone (BZ). Such an SPS is expected, and is found to contribute strongly, via a singular feature, to the density of states (DOS).

In fact, as shown in Fig. 2 and inset to Fig. 1, the DOS of bct La_2CuO_4 has a peak structure near E_F which arises from saddle points determined by the two dimensionality of the $d_{x^2-y^2}$-$p_\parallel$ band. Since this band is almost half filled, the peak in the DOS is located very close to the Fermi energy (about 0.1 eV below E_F). As a result, the DOS at E_F, $N(E_F)$, is expected to be very sensitive to the variation of the chemical potential and hence, as we shall see, to the composition x.

The general features of the valence-band structure at and below the E_F formed from a superposition of Cu d, O(1), and O(2) p orbits are reflected in the DOS (cf. Fig. 2). The strong interactions of Cu d and O(1) $p_\parallel$ in the plane are seen from the large splitting of their projected DOS into two peaks (separated by 4 eV) from O(1) and Cu. By contrast, the O(2) projected DOS yields only a single broad peak due to the weak Cu d and O(2) p hybridization.

We have seen[5] that the quasi-2D properties of the electronic structure are also supported by plots of the charge

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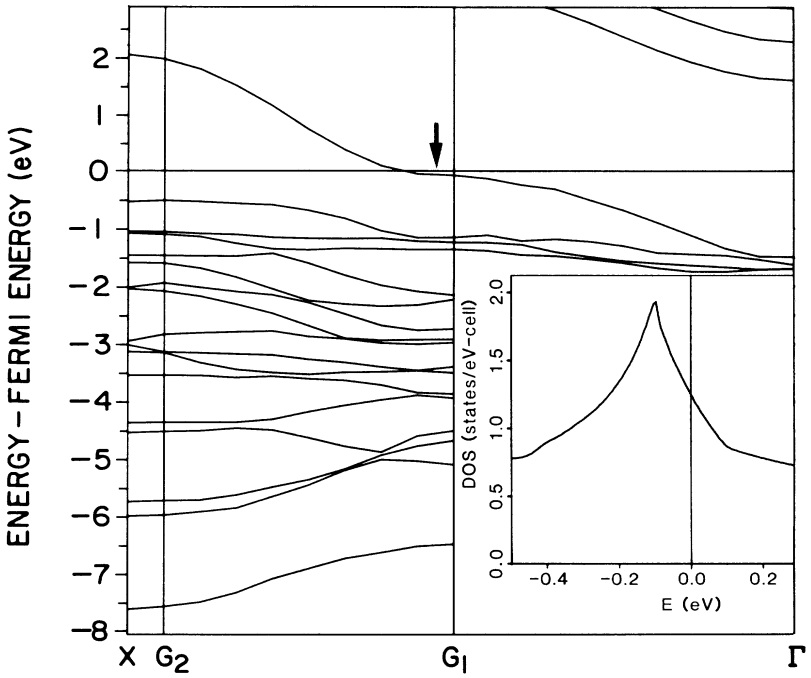

FIG. 1. Energy band structure of La_2CuO_4 along some high-symmetry directions. Note the van Hove singularity labeled by the arrow. The inset shows the van Hove singularity in the DOS.

densities of electrons at E_F. This charge density consists mainly of Cu $d_{x^2-y^2}$ and O(1) $p_\parallel$ hybridized orbitals in the plane with some additional contribution of the Cu d_{z^2} and O(2) p_z components. There is essentially no electron density around the La site at E_F. This means that the La atoms do not contribute directly to the dynamical processes involving electrons near E_F. Further, an analysis of the band structure[5] shows that the $5d$ level of La lies more than 1 eV above E_F; the $5p$ levels of La were found[5] to lie far below E_F ($\sim$15 eV). Thus, it is a fairly good approximation to consider the La atoms to be described in chemical terms as La^{3+} ions. One important consequence of this is that dilute substitution for La by trivalent magnetic rare earths, such as Pr, Nd, etc., would not affect T_c because there are no conduction electrons which can carry their magnetic pair-breaking interactions.[10]

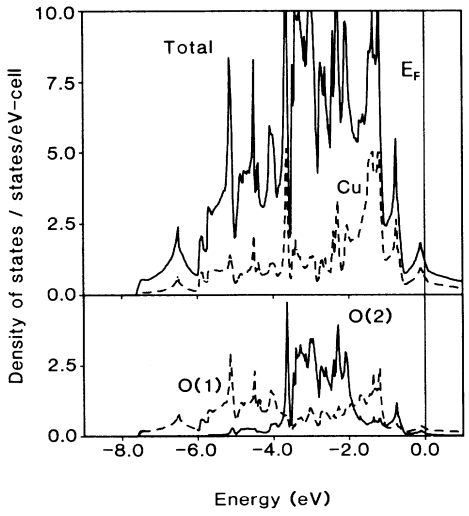

FIG. 2. Total and projected density of states for the valence bands (essentially all from Cu d–O p electrons). E_F is given for the $x=0$ composition.

The remarkable 2D nature of the electronic structure just described leads to a simple picture of the conductivity confined essentially to the metallic Cu-O(1) planes separated by insulating (ionic) planes of La-O(2). This picture is strongly confirmed by independent calculations[11] which model $La_{2-x}M_xCuO_4$ as a single slab consisting of a Cu-O(1) layer sandwiched by one La-O(2) layer on each side. (Note that such a slab has the correct stoichiometry and is charge neutral.) The electronic structure near E_F is dominated by the same single band of 2D p–d bonding character; the nesting feature (with zone boundary spanning vector) and the van Hove SPS in the DOS are reproduced with this slab approach.

In view of the results presented above, we would expect—as a first approximation—that the introduction of divalent elements (e.g., $M=$Ba, Sr, etc.) as substitutional replacements of La would not change any major feature of the band structure, charge density, DOS, etc. Thus, the use of a rigid-band approximation to treat the case of alloys, $La_{2-x}M_xCuO_4$, may be considered as a quite good first approximation when x is small (≤ 0.3). (This has been confirmed by independent virtual-crystal approximation calculations.[11]) Hence, in this spirit, the variation of composition x in $La_{2-x}M_xCuO_4$ can be taken into account simply as a change in the position of E_F, that is $E_F=E_F(x)$. Further, as stated above, since E_F lies very close to the SPS, $N(E_F)$ is extremely sensitive to the posi-

tion of E_F relative to the singular point. As a function of x, $N(E_F)$ varies from 1.2 states/eV cell at $x=0$ to 1.9 states/eV cell at $x=0.16$. This large variation in $N(E_F)$ will immediately affect a number of properties such as the magnetic susceptibility, specific heat, etc. At the critical point, however, the logarithmic singularity is not as divergent in the DOS as in the case of an exact 2D system even though the profile of the DOS looks like a logarithmic shape. This behavior is expected from the fact that there are small residual 3D interactions between the metallic Cu-O(1) layers which exhibit the quasi-two-dimensionality of the system.

As a result of this singular behavior of the DOS, many other properties of these alloys are expected to be determined by the Lifshitz–van Hove singularity. As is well known, Lifshitz[8] discussed various anomalous thermodynamic and galvanomagnetic properties of a metal that would occur when applied pressure causes E_F to pass through the SPS, i.e., a change of the chemical potential induced by pressure, $\mu=\mu(p)$. In our case, alloying with M_x additions serves to change E_F because of a change in the number of electrons n, giving us a change $\mu=\mu(n)$ or $\mu=\mu(x)$. Since the van Hove SPS is near E_F for $x=0$, lowering n (increasing x) leads to a critical composition at which the singular point and $E_F(x)$ coincide. Thus, x could be viewed as playing the role of pressure in Lifshitz's treatment. In addition, we can also introduce pressure as a second variable since, for a given x, pressure could be applied to drive E_F through the SPS again.

The crossing of the SPS by E_F with changing x (or pressure) is expected to have dramatic effects on various properties including the lattice parameters, bulk moduli, elastic constants, Young's modulus, etc.[12] Elsewhere[13] we show that variations of the lattice parameters a and c of the bct structure have already been observed for variations of x, which directly reflect the important role played by the existence of the SPS. One major effect of the van Hove singularity on the properties of the system is the anomalous behavior of T_c with varying composition x in $La_{2-x}M_xCuO_4$. With increasing x, the superconducting critical temperature T_c increases[14] rapidly from 14 K for $x\simeq 0.05$ to a maximum of 37 K for $x\simeq 0.2$, but then drops sharply for larger x values. Such anomalies in T_c under pressure have been treated[15] by using a modified BCS equation. As seen above, in contrast to their 3D van Hove singularity,[15] which gives $\delta N(E)\propto |E_F-E|^{1/2}$, the singular behavior of the DOS in our quasi-2D system results in the logarithmic-type (i.e., strong) change of the DOS. Thus, we expected that the correction δT_c, due to the singular part of $N(E)$ will be much larger than that obtained previously for the 3D case. In the 3D case the correction from the nonanalytic (i.e., singular) point is found to be small, of the order $\sim h\omega_D/E_F$ with ω_D =Debye frequency. In our case, the major change of $N(E)$ as a function of x may well determine the observed characteristic dramatic variation of T_c with x.

From the BCS theory of superconductivity, the transition temperature T_c is determined by the pairing interaction strength, $\lambda=N(E_F)V$ and V is the pairing potential arising from the electron-phonon interaction. Considering the transition temperature T_c as a function of x, we can write down the dependence of T_c on x as follows:

$$\frac{dT_c}{dx}=\frac{\partial T_c}{\partial N(E_F)}\frac{dN(E_F)}{dx}+\frac{\partial T_c}{\partial V}\frac{dV}{dx}\ . \tag{1}$$

This assumes that the average phonon frequency remains constant. When

$$\left|\frac{1}{N(E_F)}\frac{dN(E_F)}{dx}\right|\gg\left|\frac{1}{V}\frac{dV}{dx}\right|\ ,$$

the change ΔT_c will be determined by the change of $N(E_F)$. Since the change of Fermi-surface topology due to the SPS has a small (in our terms) effect on the phonon spectrum,[15] the variation of the pairing potential V will be small.[16] (Indeed, the frozen phonon calculations, which yield a high frequency for the breathing mode and a large electron-phonon interaction energy, find little dependence on Fermi-surface nesting.[11]) Under these approximate conditions, the change in T_c with composition x is associated with a change of $N(E_F)$. In fact, recent reports[14] show a large variation of T_c vs x which rises sharply from 0 K at $x<0.03$ to 22 K at $x=0.08$, hits a maximum at $x\simeq 0.15$, and then drops off sharply. These results are very consistent with our picture. Thus, it is clear that the strong variation in $N(E_F)$, derived from the quasi-2D van Hove singularity (cf. Fig. 1, inset), plays a dominant role in the anomalous behavior of T_c as a function of x.

One of the traditional devices for obtaining information about the interaction driving the superconductivity is to measure the electronic contribution to the specific heat γ, and to obtain the dressed DOS at E_F, $N^\gamma(E_F)$. Writing $N^\gamma(E_F)=N(E_F)(1+\lambda)$, where $N(E_F)$ is the noninteracting (or band) DOS, one can, from the measured $N^\gamma(E_F)$ and calculated $N(E_F)$, obtain the interaction parameter λ which plays an essential role in superconductivity. Generally, λ is thought to arise from electron-phonon $\lambda_{e\text{-ph}}$, electron-electron $\lambda_{e\text{-}e}$, and spin-fluctuation contributions λ_{sp} (expected to be small in these wide band materials).

Since λ is so important, a number of groups have attempted the measurement of $N^\gamma(E_F)$ using a variety of techniques. Unfortunately, the difficulty of the measurement, particularly on the powders available so far, has resulted in a variety of values for $N^\gamma(E_F)$. In turn, the use of our calculated $N(E_F)$ values results in a range of derived values for λ. Further, since, as we have seen, $N(E_F)$ is a strong function of divalent composition x—and of the oxygen vacancy defect concentration—care is required in relating a measured $N^\gamma(E_F;x)$ to the corresponding theoretical $N(E_F;x)$ to derive $\lambda(x)$. A further note of caution is to be sounded: Our calculated values of $N(E_F;x)$ are obtained using a rigid-band approximation to the results obtained in a local-density calculation for low-temperature lattice parameters measured[17] for a Ba composition $x=0.15$. Calculations of $N(E_F)$ for varying measured lattice constants (corresponding to the varying x values) are in progress.

With these caveats, we may cite some of the λ values we have obtained from measured values of γ (in mJ/mole K^2) known to us. (i) From their dH_{c2}/dT (and resistivity) results (for $x=0.15$), Kwok *et al.*[18] obtained $\gamma_{\min}=4.9$

(dirty limit) and $\gamma_{max}=7.3$ (clean limit) which gives us $\lambda=0.07$ and 0.59, respectively. (ii) Battlogg *et al.*[19] cite an average of three different experiments (on $x=0.15$), $\gamma_{BCS}=6\pm1.5$, which results in $\lambda=0.3\pm0.3$. (iii) From high-field measurements on the dH_{c2}/dT, Foner *et al.*[20] obtained (for $x=0.15$ and 0.20) $\gamma=6.275$ (at the resistance midpoint) and 14.8 (at the resistance drop onset temperature); the corresponding λ's have a large range, from 0.39 to 2.22. (iv) The results of Panson *et al.*[21] (for $x=0.2$) yield a γ value (2.7 ± 0.1) which is far below our bare value. (v) Experiments by Thiel *et al.*[22] at a sample with $x=0.17$ (just at the SPS) derive from dH_{c2}/dT and a resistivity of 353 $\mu\Omega$ cm, a $\gamma=6.3$ and hence, $\lambda=0.39$. This range of γ values reflects the difficulties in the measurements cited above. Excluding the upper value of Foner *et al.*,[20] one seen a consistent set of λ values emerge, namely, $\lambda=0.3\pm0.3$. This result indicates that one may well be in the weak coupling limit.

As stated above, a recent frozen phonon calculation[11] found that [due to the strong Cu d–O(1) p bonding] the optic breathing mode has a very high frequency ($\Theta_D=1100$ K). If one uses the measured T_c (~40 K) and this calculated Θ_D in a simple BCS equation with λ and μ^*, one finds that $\lambda-\mu^*=0.3$, or well within the range of values for λ given above. We can also estimate theoretically the contribution from the optic breathing mode to λ. Using $\langle u^2\rangle=\hbar/2M\omega_q$, we obtain an rms phonon displacement $\simeq0.04$ Å. The electron-phonon interaction matrix element can be calculated from the electronic band splitting near the phonon BZ boundary due to the phonon-induced O displacement; a deformation potential $\simeq3$ eV/Å is obtained for states with Cu $d_{x^2-y^2}$–O $p_{x,y}$ character near E_F. These quantities, together with the calculated $N(E_F)$, give λ_q (breathing mode) $\simeq0.25$. Notice that, despite its high frequency, the breathing mode also makes a sizable contribution to the Fermi-surface averaged value of λ.

Further, using our calculated v_F values, a crude (order of magnitude) estimate may be made of the upper critical fields, $H_{c2\parallel}$ and $H_{c2\perp}$ and coherence lengths $\xi_\parallel$ and $\xi_\perp$. While not appropriate, we use the clean limit[23] since we have no information about the scattering length. We find that $\xi_\parallel\gtrsim130$ Å, $\xi_\perp\simeq1$ Å, and $H_{c2\parallel}\simeq200$ T, $H_{c2}\simeq2$ T —clearly indicating the effects of the strongly 2D nature of the calculated band structure.

Finally, single-crystal measurements are essential for obtaining more meaningful values of the various parameters discussed in this paper.

Note added. Since submission of this paper, there appeared another paper[24] with a similar band structure to that of Ref. 5.

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. **26**, L1 (1987); H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *ibid.* **26**, L123 (1987).
[3]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).
[4]R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).
[5]Jaejun Yu, A. J. Freeman, and J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).
[6]H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984); E. Wimmer *et al.*, *ibid.* **24**, 864 (1981).
[7]J.-H. Xu, T. J. Watson-Yang, Jaejun Yu, and A. J. Freeman, Phys. Lett. A **120**, 489 (1987).
[8]I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys. JETP **11**, 1130 (1960)].
[9]L. Dagens, J. Phys. F **8**, 2093 (1978).
[10]As apparently recently observed by C. Kimball *et al.* (unpublished).
[11]C. L. Fu and A. J. Freeman, Phys. Rev. B **35**, 8861 (1987).
[12]M. I. Kaganov, Usp. Fiz. Nauk **145–147**, 507 (1985) [Sov. Phys. Usp. **28**, 257 (1985)].
[13]A. J. Freeman, Jaejun Yu, J. Jorgensen, D. Hinks, and D. W. Capone II (unpublished).
[14]S. Kanbe, K. Kishio, K. Kitazawa, K. Fueki, H. Takagi, and S. Tanaka, Chem. Lett. (to be published).
[15]R. J. Higgins and H. D. Kaehn, Phys. Rev. **182**, 649 (1969).
[16]A crude calculation of the electronic contribution to λ, based on the rigid muffin-tin approximation for varying x, supports the argument that

$$\left|\frac{1}{V}\frac{dV}{dx}\right|$$

is small relative to

$$\left|\frac{1}{N(E_F)}\frac{dN(E_F)}{dx}\right|,$$

assuming the average phonon frequency is constant.
[17]J. D. Jorgensen *et al.* Phys. Rev. Lett. **58**, 1024 (1987).
[18]W. K. Kwok, G. W. Crabtree, D. G. Hinks, D. W. Capone II, J. D. Jorgensen, and K. Zhang, Phys. Rev. B **35**, 5343 (1987).
[19]B. Batlogg, A. P. Ramirez, R. J. Cava, R. B. van Dover, and E. A. Rietman, Phys. Rev. B **35**, 5340 (1987).
[20]S. Foner, T. P. Orlando, E. J. McNiff, Jr., J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, Phys. Rev. B **35**, 7249 (1987).
[21]A. J. Panson, G. R. Wagner, A. I. Braginski, J. R. Gavaler, M. A. Janocko, H. C. Pohl, and J. Talvacchio, Appl. Phys. Lett. **50**, 1104 (1987).
[22]J. Thiel, S. Song, K. Poepplemeier, J. B. Ketterson, and A. J. Freeman (unpublished).
[23]W. E. Lawrence and S. Doniach, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, 1970,* edited by E. Kanda (Keigaku, Tokyo, 1971), p. 361.
[24]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).