Pressure-Induced Hole Doping of the Hg-Based Cuprate Superconductors

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We investigate the electronic structure and the hole content in the copper-oxygen planes of Hg-based high T_c cuprates for one to four CuO_2 layers and hydrostatic pressures up to 15 GPa. We find that with the pressure-induced additional number of holes of the order of $0.05e$ the density of states at the Fermi level changes by approximately a factor of 2. At the same time, the saddle point is moved to the Fermi level accompanied by an enhanced k_z dispersion. This finding explains the pressure behavior of T_c and leads to the conclusion that the applicability of the van Hove scenario is restricted. By comparison with experiment, we estimate the coupling constant to be of the order of 1, ruling out the weak coupling limit.

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In the high temperature superconductors, the critical temperature strongly depends on the number n of CuO_2 layers per unit cell. In particular, an increase of the transition temperature with increasing n has been verified within the different cuprate families, such as the Bi-, Tl-, or Hg-based compounds. Although it seemed tempting to add more and more such CuO_2 layers to the crystal structure, there is a limit in that for $n > 3$ the superconducting properties become worse, i.e., T_c decreases again. Besides the composition, pressure is an important tool to enhance the transition temperature. This effect is most pronounced for the Hg-based cuprates [1], which still hold the world record in T_c being 97 K for $n = 1$ and ambient pressure, and even 164 K for $n = 3$ at 30 GPa [2,3]. Therefore, this system is best suited to simultaneously study both effects.

In this Letter, we report on the electronic properties of $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ as a function of composition, i.e., $n = 1, 2, 3, 4$, and hydrostatic pressure, investigated by first-principles calculations. Special emphasis has lead to the question of how the charge carriers are redistributed leading to an increase of the hole concentration in the CuO_2 layers, which are responsible for the superconducting current. At the same time, the density of states (DOS) at the Fermi level is considered to shed light on the role of the van Hove singularity (vHS) [4] for the superconductivity and to estimate the coupling constant.

All calculations, which are based on density functional theory, have been carried out with the full-potential linearized augmented plane wave method utilizing the WIEN2K code [5]. The atomiclike basis set used in the atomic spheres around the nuclear positions [6,7] allows for an analysis of the electronic charge in terms of atomic origin and for a decomposition of the charge according to its orbital momentum l. Therefore, the decrease of the corresponding occupation number can be interpreted as the creation of a certain amount of holes of the particular character. Below, the CuO_2 layers will be analyzed that way. The most important orbitals are Cu-$d_{x^2-y^2}$ and O-p_x forming pd—σ bonds. Note that the O-p_y orbital of the second oxygen neighbor is equivalent to the O-p_x orbital of the other oxygen due to symmetry. For all our calculations, the crystal structures have been relaxed in terms of lattice parameters and atomic positions as determined and discussed in detail in Ref. [8]. This procedure makes the calculations not rely on experimental crystalline data. The latter is important for studying the pure dependence of the electronic properties on pressure or n, since the measured samples usually include some excess oxygen and can be strongly Hg deficient [9].

Figure 1 depicts the number of holes created in the Cu-$d_{x^2-y^2}$ orbitals when pressure is applied. Before discussing the details, it should be noted that for all compounds and pressures the atomic sphere radii, chosen as 2.1, 2.3, 1.9, 1.2, and 2.0 a.u. for Hg, Ba, Cu, O, and Ca, respectively, in which the electronic charge is analyzed, have been kept constant. This means that a bigger fraction of the crystal volume and hence electronic charge is lying inside the sphere when pressure is applied/increased. Therefore, the number of pressure-induced holes can be regarded to be somewhat underestimated by our pressure calculations. Nevertheless, it can be stated that there is a pronounced pressure effect on the orbital occupation numbers of copper, whereas there is hardly any change in the corresponding oxygen O-p_x charges [8]. This is in contrast to the doping-induced holes [10] which are found not only at the copper sites, but also, to some extent, on the oxygen positions.

Let us first focus on the partial charges at ambient pressure. When changing the composition, the Cu-$d_{x^2-y^2}$ occupation number changes from 1.4336 for $n = 1$ to 1.4414 for $n = 2$, 1.4421 (1.4386) for $n = 3$, and 1.4413 (1.4380) for $n = 4$. The numbers in parentheses refer to the inequivalent copper positions occurring for the three

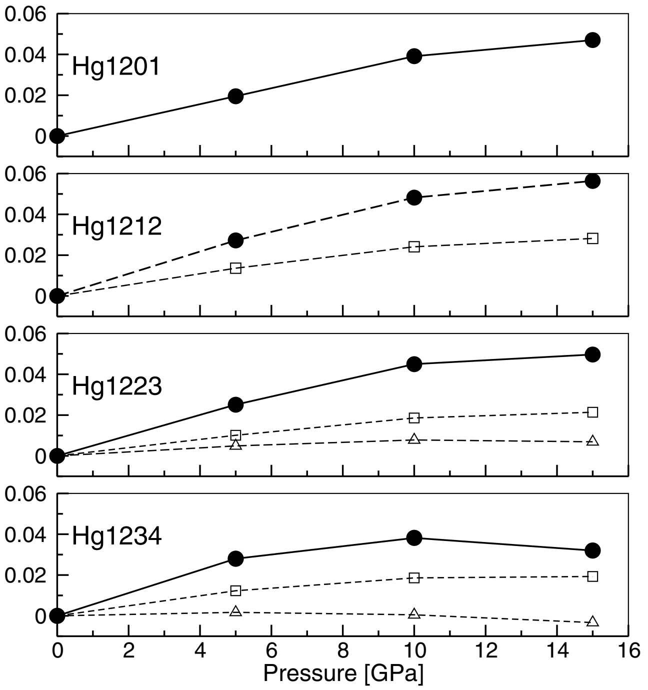

FIG. 1. Number of pressure-induced holes (in units of electrons) for the Hg-based cuprates, Hg1201, Hg1212, Hg1223, and Hg1234 for pressures up to 15 GPa. The values are taken with respect to ambient pressure for each material. The solid circles correspond to the total number of holes created per unit cell, whereas the open symbols (triangles for the innermost layer and squares for the outer layers) reflect the situation in a particular layer. The symbols indicate the calculated data points, while the lines serve to guide the eye.

and four layer compounds and indicate an inhomogeneous hole distribution that concerns the different CuO_2 layers within one unit cell. Upon applying pressure, the number of holes increases with a paraboliclike shape, which at 15 GPa is close to its maximum for n up to three. Only for $n = 4$ is there already a slight decrease in the highest pressure range. An important fact is that the amount of pressure-induced charges per site decreases for higher n. In particular, the innermost layers (marked by triangles in Fig. 1) do not gain more holes with pressure beyond $n = 3$. Only the total amount of holes per cell created for a certain pressure value is similar in all the compounds, i.e., when the contributions from different layers are summed up, weighted by their multiplicity.

All these findings are fully concomitant with the superconducting transition temperature [9]: Experimentally, the enhancement of T_c for n up to three with pressure is approximately 15–20 K between 0 and 15 GPa; i.e., it is nearly independent of n. Only for $n = 4$ is the curve somewhat flatter. Exactly the same trend is found for the number of pressure-induced holes. The inhomogeneous charge distribution among the different layers also provides an explanation for the limited T_c since the inner layers do not gain any more holes by further insertion of CuO_2 planes.

The fact that T_c scales with the number of charge carriers does not, however, provide an explanation for the origin of superconductivity. Although the amount of holes in the cuprate planes is an important quantity, its knowledge does neither lead to a conclusion about the pairing mechanism nor about the coupling strength to the mediating quasiparticles. Therefore, the question arises what the role of the bands and the density of states around the Fermi level is. In this context, the van Hove scenario has been frequently invoked. Indeed, the most precise calculations for the band structure of $YBa_2Cu_3O_7$ [11] exhibit a saddle point (usually referred to as a vHS) pinned to the Fermi level, and the same is true for $La_{2-x}Ba_xCuO_4$ [12] and $HgBa_2CuO_{4+\delta}$ at optimal doping [10].

Here, we will assess this possibility for the Hg-based compounds under pressure by performing self-consistent calculations for all pressure values to obtain the corresponding electronic structures. Thereby we observe two effects: First, upon applying pressure, the dispersion in the k_z direction is strongly increased. In Hg1201, the bandwidth of the pd—σ band along XR is changed from 0.12 to 0.29 eV between 0 and 10 GPa, which corresponds to a factor of 2.5. Second, at the same time, the ratio of hopping matrix elements t'/t decreases by 6%, where t' and t denote the in-plane matrix elements of O-O and Cu-O hopping when mapping the band structure to a simple tight binding model. These two effects lead to an asymmetry in the location of the vHS with respect to the Fermi level for different k_z values. This can be seen in Fig. 2, where the pressure dependence of the Hg1201 band structure around E_F along the two high symmetry lines ΓX and ZR is depicted. Upon applying pressure, the shoulder between Z and R clearly moves up toward the Fermi level, intersecting it at around 10 GPa. Along ΓX the band is pushed up as well, thereby getting steeper but staying below E_F in the entire pressure range. As a result, the vHS is broadened when it arrives at the Fermi level. Thus, we have found the vHS to be pinned to the Fermi level within a certain region of the Brillouin zone (between ΓX and ZR) at high pressures, which could be related to the high and rather weakly pressure-dependent T_c in a pressure range between 10 and 20 GPa.

These findings also show up in the density of states depicted in Fig. 3. For Hg1201, the shoulder in the DOS is located at −0.5 eV but moving up toward E_F with pressure, where the density of states at the Fermi level N_0 is slowly varying only for higher pressure values (see Fig. 4). For $n = 3$, the situation is the same, while for $n = 2$ and 4 the vHS crosses E_F between ZR and stays below E_F along ΓX. Concerning the magnitude of the DOS, the following is interesting to note: N_0 is getting larger with the number of layers, where the pressure-induced increase is nearly the same for $n = 1$, 2, and 3. The reason for the latter

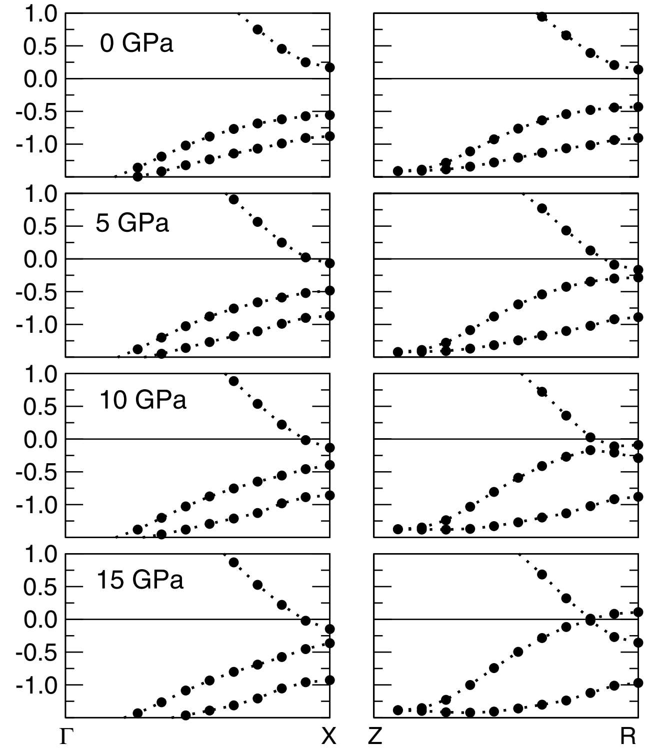

FIG. 2. Band structure of Hg1201 along the high symmetry lines ΓX and ZR for different pressure values. The black, solid circles mark the calculated points, where the dotted lines serve to guide the eye. The Fermi level is set to zero and indicated by a horizontal line, and the energy is given in eV.

fact is that with additional CuO_2 layers the corresponding bands are not fully degenerate but exhibit a certain splitting which does not allow all the corresponding shoulders (vHS) to sit at E_F at the same time. Thus, the pressure-effect on the DOS is independent of the number of layers, at least up to $n = 3$. This trend goes hand in hand with the number of holes as well as with the critical temperature. Only for $n = 4$ is the pressure-effect less pronounced, since at ambient pressure N_0 does not fall into a local minimum as is the case for the other compounds.

We want to point out that the self-consistent treatment is crucial for understanding the changes of the band structure under pressure. For example, when using the rigid band approximation to estimate the pressure-induced number of holes necessary to push the vHS to the Fermi level, as it was proposed first by Novikov *et al.* [13], this quantity being of the order of $0.5e$ is overestimated by about an order of magnitude (see Fig. 2).

Knowing, on the one hand, the pressure dependence of N_0 for the four compounds as a result of our calculations and the corresponding experimentally measured T_cs on the other hand, one can try to estimate the effective dimensionless coupling constant $\lambda = VN_0$, assuming a BCS-like behavior is valid for the weak coupling for any type of the intermediate boson, $T_c \sim \omega_B \exp(-1/\lambda)$. Here, ω_B is the frequency of the mediating boson, and V characterizes the coupling strength. It should be noted here that the DOS does not necessarily have to be assumed to be constant near the Fermi level on the ω_B scale, but it turned out to be approximately the case (Fig. 3) and thus can be used for such an estimation. There are, however, several problems which hamper a quantitative comparison between theory and experiment. (i) The main concern comes from the fact that T_c has been measured on samples which include a doping concentration close to optimal doping. This doping could be considered as an unknown chemical pressure. On the contrary, the calculations have been performed for the undoped material. (ii) There are big uncertainties in the experimental data regarding defects and nonstoichiometry of the samples. (iii) When dealing with compounds with more than one layers, it is unclear how their contributions enter T_c.

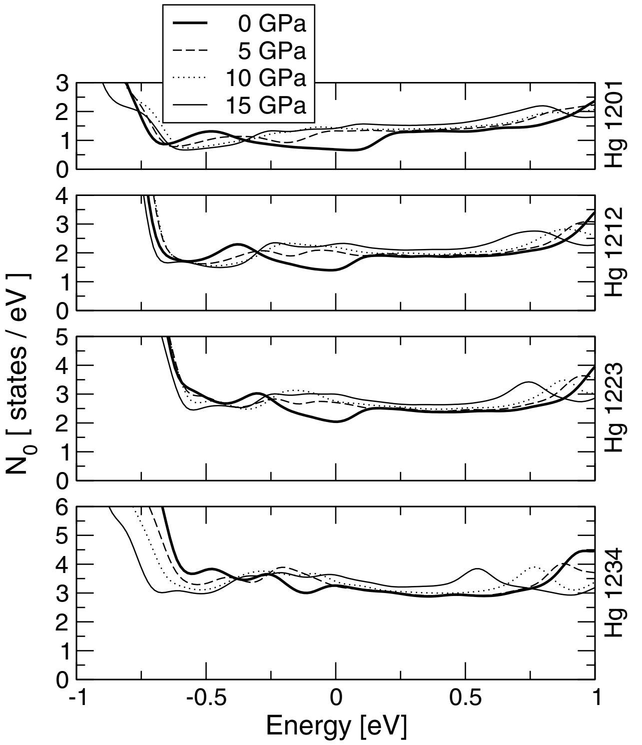

FIG. 3. Densities of states N in states per eV and unit cell of Hg1201, Hg1212, Hg1223, and Hg1234 for pressure values of 0, 5, 10, and 15 GPa.

Despite all these uncertainties, conclusions are nevertheless possible. First, from all calculations performed to investigate doping as mentioned before for $YBa_2Cu_3O_7$ [11], $La_{2-x}Ba_xCuO_4$ [12], and $HgBa_2CuO_{4+\delta}$ [10], we know that at optimal doping the saddle point is pinned to the Fermi level. Since in Hg1201 the vHS reaches E_F at approximately 5 GPa, we interpret this value as the effective "chemical" pressure corresponding to optimal doping in the sense that both the optimal doping and this pressure lead to similar changes in the electronic

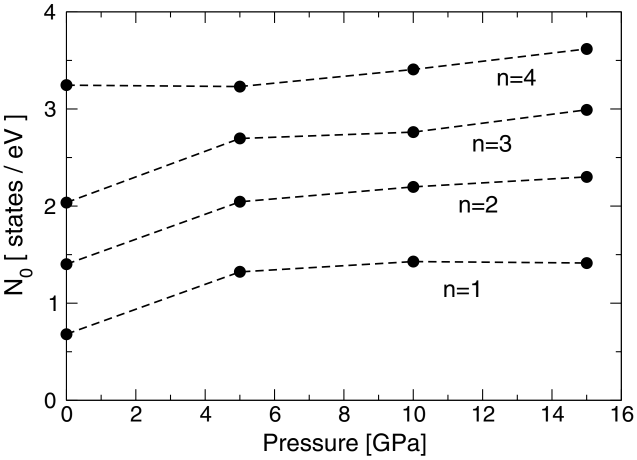

FIG. 4. Densities of states at the Fermi level N_0 in states per eV and unit cell in Hg1201, Hg1212, Hg1223, and Hg1234 for pressure values of 0, 5, 10, and 15 GPa.

band structure in the vicinity of the Fermi level, which are important for superconductivity. The changes of T_c due to pressure occur on top of the doping-induced T_c, i.e., are of the order of 10%–20%. The same is observed in N_0 when increasing pressure above 5 GPa, as shown in Fig. 4. From a comparison of the pressure-induced change of T_c with the change of N_0, we can estimate $\lambda = \Delta N_0/\Delta T_c \times T_c/N_0$ being of the order of 1. Taking into account a possible pressure enhancement of ω_B can only increase this estimated value. Therefore, we can rule out the BCS-like weak coupling approaches.

Second, we want to comment on the van Hove scenario. We find that it is not the driving force for boosting T_c in the sense that it never shows up as a sharp peak in the density of states at the Fermi level. At ambient pressure, there exists only a saddle point in the band structure, i.e., a rather broad feature in the density of states which is further considerably broadened when pressure is applied. Thus, the effect of a nonuniform density of states near the Fermi level, which was supposed to be important to enhance T_c [14] in comparison with standard BCS theory, is not applicable in this case. Nevertheless, this saddle point plays an important role as it is pinned to the Fermi level at optimal doping. The pressure effect on T_c can be traced back to the above discussed pressure-induced z dispersion and the corresponding changes in the hopping matrix elements.

Summarizing our results, we find the hole content in the CuO_2 planes to increase as a function of pressure by approximately 0.05 electrons, going from ambient pressure to 15 GPa. These changes in the hole concentration are accompanied by a considerable gain in the density of states at the Fermi level arising due to the movement of the saddle point up to and even through the Fermi level. The latter effect is caused by an increase in the z-axis dispersion due to pressure. We find the effect of optimal doping to be equivalent to applying a pressure of approximately 5 GPa. On top of this, the increase in the density of states is of the order of 10% in parallel to the enhancement of T_c, which is of the same order of magnitude. From this comparison we conclude that superconductivity in this cuprate family is described by the intermediate to moderately strong coupling regime, i.e., λ being of the order of 1. The saddle point, often referred to as a vHS, does not show up as a peak in the density of states, making models based on a nonuniform density of states not applicable to high T_c cuprates.

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