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Jansen, L.; Block, R.

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Quantitative analysis of superconductivity in the Hg-cuprates. Comparison with the Tl_2 -series

Laurens Jansen^a, Ruud Block^b

^a*c/o Theoretische Physik, ETH-Hönggerberg, 8093 Zürich, Switzerland*

^b*J.H. van't Hoff Institute, University of Amsterdam, 1018 WV Amsterdam, The Netherlands*

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Abstract

A quantitative analysis is developed for the effect of external pressure on critical temperatures in $Hg(N)$ - and $Tl_2(N)$ -superconductors with $N = 1, 2$, and 3 CuO_2 layers per molecular unit, and with chemical composition $HgBa_2Ca_{N-1}Cu_NO_{2N+2+\delta}$ and $Tl_2Ba_2Ca_{N-1}Cu_NO_{2N+4+\delta}$, respectively. As in earlier work, Cooper pair formation is assumed to arise from indirect exchange pairing between conduction electrons via closed-shell oxygen anions (O^{2-}), in a s-wave BCS formalism. The exchange coupling is obtained as a function of three parameters α , β , and κ , with α and β (Gaussian) parameters in the wavefunction for the oxygen valence band and the conduction electrons, respectively, and $\kappa = bk_F/\alpha^{1/2}$, with b a materials constant for the cuprates; k_F is the length of the Fermi vector. Comparison is also made with experiments in which, for the Tl_2 series, pressure is applied (or changed) either just above T_c or at room temperature. Agreement with experimental results is quantitative throughout; in particular, the high T_c values of 154 K (for $Hg(N=2)$) and ≈ 160 K ($Hg(N=3)$) are quantitatively reproduced, at the pressures observed. They are due to two-dimensional characteristics of superconductivity in these systems. The anomalous behavior of $T_c(P)$ in the $Tl_2(N)$ compounds with pressure applied at ambient temperature is found to result from pressure-induced diffusion of oxygen anions from the $(Tl-O)_2$ bilayers towards the CuO_2 layers. Neither van Hove singularities nor pressure-induced changes of the hole concentration in the CuO_2 layers are found to play a role in superconductivity of these compounds.

1. Introduction

Superconductivity up to 134 K (at ambient pressure), thus well above the original record-high of 125 K established in 1988 [1] for the $N = 3$ member of the homologous series $Tl_2Ba_2Ca_{N-1}Cu_NO_{2N+4+\delta}$, was found by Schilling et al. [2] in the new cuprate family $HgBa_2Ca_{N-1}Cu_NO_{2N+2+\delta}$ and attributed to the $N = 3$ member of the series (we will use the short notation $Tl_2(N)$ and $Hg(N)$, respectively). Somewhat earlier, Putilin et al. [3] found $T_c = 94$ K for $Hg(N = 1)$, again several degrees higher

than the T_c of 85–90 K in $\text{Ti}_2(N = 1)$, later followed by $T_c = 121$ –127 K in $\text{Hg}(N = 2)$ [4] (see also [6]), compared with 112–118 K for the $N = 2$ member of the Ti_2 family. These findings initiated several analyses also of other properties of the $\text{Hg}(N)$ series. For example, Schilling et al. [5] measured on $\text{Hg}(N = 3)$ a critical current density of $\geq 5 \times 10^6 \text{ A cm}^{-2}$ at 10 K, and of $\geq 2 \times 10^4 \text{ A cm}^{-2}$ at 75 K, in a magnetic field of 1 T. The irreversibility line is found to approach that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and of $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$. Antipov et al. [6] synthesized, in addition to $\text{Hg}(N = 3)$, also the $N = 4$ member of the series, finding $T_c < 132 \text{ K}$ (126 K), implying that after 3 CuO_2 layers per unit cell, the critical temperature decreases, in striking parallel with the Ti_2 -series where T_c drops to 116 K for $N = 4$ [7].

Also the crystal structures of $\text{Hg}(N)$ and $\text{Ti}_2(N)$ are similar (tetragonal; in some examples [8]¹ a slightly orthorhombic phase for $N = 3$ is also found). The length of the a -axis changes little with N , whereas that of the c -axis closely follows $C_N = 6.3 + 3.2N (\text{\AA})$, identical with that for the Ti_1 -series, with only one Ti-O layer per molecular unit and a maximum T_c of 121 K for $N = 4$ [9,10]. However, the latter series is less stable, and less stoichiometric, than the $\text{Ti}_2(N)$ family (its first member is hardly a superconductor). We will in what follows only compare the $\text{Hg}(N)$ and $\text{Ti}_2(N)$ series, for which properties (at ambient pressure) are much more alike. The corresponding relation for the $\text{Ti}_2(N)$ series (inversion symmetry) is $C_N/2 = 8.2 + 3.2N$.

It has recently been found [11] that moderate pressure (4.2 GPa) increases T_c of the $\text{Ti}_2(N = 3)$ system to 133 K, i.e. the same value as for $\text{Hg}(N = 3)$ at ambient pressure. A distinct drop in electrical resistivity at surprisingly high temperatures has been observed for the $\text{Hg}(N)$ series at high pressures, even reaching 164 K for $N = 3$ at $P = 31 \text{ GPa}$ [12], after an initial report of $T_c = 153 \text{ K}$ at $P = 15 \text{ GPa}$ [8]. We will analyze these phenomena in a later section of the present paper.

Of prime importance for a comparison between theoretical and experimental results on the pressure dependence of T_c is the slope dT_c/dP at ambient pressure. An excellent review of the already numerous experiments on the $\text{Hg}(N)$ cuprates was recently published by Klehe et al. [13], who analyzed different methods and the reliability of results obtained. These authors, utilizing a He-gas compressor system and purely hydrostatic pressure, find for $\text{Hg}(N = 2)$ an initial slope $dT_c/dP = +1.80 \pm 0.06 \text{ K/GPa}$ (at $T_c = 126.6 \text{ K}$), for the $N = 3$ system $+1.71 \pm 0.05 \text{ K/GPa}$ (at $T_c = 133.9 \text{ K}$). Using the same method, Klehe et al. [14] had earlier established a value $dT_c/dP = +1.72 \pm 0.05 \text{ K/GPa}$ (at $T_c = 98 \text{ K}$) for $N = 1$. Compared with other cuprate superconductors these values are not excessive (e.g. for $\text{YBa}_2\text{Cu}_4\text{O}_8$ $dT_c/dP \approx +5.5 \text{ K/GPa}$), but in the $\text{Hg}(N)$ cuprates a practically constant slope extends to high pressures, causing a maximum T_c well beyond 150 K for $N = 2$ and especially $N = 3$. For $\text{Ti}_2(N = 3)$ the initial $dT_c/dP \approx 1.75 \text{ K/GPa}$, but $T_c(P)$ reaches a maximum of only 133 K at $P = 4.2 \text{ GPa}$

¹ Orthorhombicity of $\text{Hg}(N = 3)$ is also reported in [16].

[11]. The explanation of these phenomena constitutes a severe test on the validity of theoretical approaches to superconductivity in the $\text{Hg}(N)$ and $\text{Tl}_2(N)$ cuprates.

Assuming electrostatic balance for nominal composition of the $\text{Hg}(N)$ compounds, i.e. for $\delta = 0$, the (hole) dopant is the excess oxygen, situated at the site O(3) in the plane of the Hg atoms (ions). Values of δ are expected to increase with the number N of CuO_2 layers per molecular unit and to depend sensitively on the measured transition temperature (sample preparation). We give only results from high-resolution neutron-diffraction analyses: $\delta \approx 0.06$ at $T_c = 95$ K for $N = 1$ [15]; $\delta \approx 0.22$ at $T_c = 128$ K for $N = 2$ [16] and $\delta \approx 0.26$ at $T_c = 134$ K for $N = 3$ [16].

The majority of theoretical analyses concerns band structure calculations for (electronically) two-dimensional systems, starting with Singh [17] for $\text{Hg}(N = 1)$, using a linear combination of augmented plane waves in a local-density approximation (LAPW-LDA), followed by a similar analysis for $N = 3$ [18]. Novikov and Freeman [19,20] employ a full-potential linear muffin-tin orbital method (FLMTO), applied to $N = 1, 2$, and 3; a similar approach was adopted by Rodriguez et al. [21]. A common result of these analyses is that an antibonding band, arising from hybridization of Hg p- and d-orbitals with apical-oxygen (O(2)) states, is obtained which lies slightly above the Fermi level for $N = 1$, but crosses E_F for $N = 2$ and 3, opening the possibility of “self-doping” in these latter cases.

Novikov and Freeman [19,20] suggest an essential contribution to the density-of-states (DOS) at E_F by van Hove singularities (vHs), into which, they conjecture, E_F can be moved by doping or pressure. Similar ideas were forwarded by Freeman et al. [22,23] in the early phase of high- T_c superconductivity. We comment on the possible relevance of vHs for cuprate high- T_c superconductivity in the final section of the present paper.

It was mentioned earlier that the T_c of $\text{Tl}_2(N = 3)$ can be raised from 128.5 K at $P = 0$ to a maximum of 133 K at $P = 4.2$ GPa [11], the same critical temperature as for $\text{Hg}(N = 3)$ at *ambient* pressure. This observation regarding two very similar cuprate systems raises a number of general questions on cuprate superconductivity, of which we mention one aspect already here. If, as the authors of [11] assume, oxygen acts as a hole dopant only, and if pressure increases the hole concentration in the CuO_2 layers, then the observed raise (to 133 K) poses a problem. The authors conjecture, instead, that pressure in this case diminishes the “non-uniformity” in hole distribution between the three CuO_2 layers (two outer layers and one inner layer), resulting in an increase of T_c with P (through proximity coupling). The somewhat larger Cu-apical oxygen distance in $\text{Hg}(N = 3)$, 2.79 Å, compared with $\text{Tl}_2(N = 3)$, 2.65 Å, is then interpreted as a tendency towards a more “uniform” charge distribution between the CuO_2 layers in the Hg-compound, resulting in a somewhat higher critical temperature. However, the distinctly different critical temperatures between the $\text{Hg}(N)$ and Tl_2 series also for $N = 1$ and $N = 2$ invalidate such an approach.

Chen et al. [24] deduce, from measurements of T_c as a function of pressure in Hg ($N = 2$), evidence for the possible occurrence of a “van Hove singularity” in the

spectrum of this compound. For as-synthesized samples, with $T_c(P=0) = 111$ K, a slope $dT_c/dP = 2.2$ K/GPa is measured up to the highest applied pressure (1.8 GPa). For oxygen-annealed samples, with $T_c(P=0) = 117$ K, dT_c/dP is practically the *same* as before up to 0.4 GPa, at which point a break in the slope occurs to half this value. Assuming that pressure induces hole transfer to the CuO_2 layers, this breakpoint would be reached at a lower pressure for higher oxygen content, possibly explaining why for lower oxygen content (fewer holes) the break is not observed up to the highest pressure applied (1.8 GPa). We will analyze this phenomenon in Section 5.2.

It is concluded that at present there exists no quantitative basis for a theoretical interpretation of critical temperatures, and their pressure dependence, of the new $\text{Hg}(N)$ superconductors. Also, the origin of the differences with those properties of especially the Tl_2 series is not understood.

The present analysis aims at a quantitative elucidation of these aspects, on the basis of an earlier proposed indirect-exchange mechanism of pairing between conduction electrons via the filled oxygen valence band in the cuprates. The indirect-exchange interaction arises because of the Pauli principle (antisymmetrization) applied to the system of (one-electron) conduction states and valence-band states in case the wavefunctions of these subsystems overlap to some extent. For the high- T_c cuprates there exists abundant evidence (e.g. from photoemission experiments) that such is the case, i.e. the conduction (one-electron) wavefunctions have some valence-band component (mixing).

The method was originally developed for low- T_c metals [25], was later extended to high- T_c cuprates [26,27]. Of recent applications we mention an analysis of the relationship between doping, T_c and dT_c/dP in high- T_c cuprates [28], which is directly applicable to the problem at hand. In view of the short-range character of exchange interactions, the valence-band states are transformed to Wannier functions at the sites of the oxygen anions, representing closed-shell (i.e. diamagnetic) units. In the next section we summarize the main aspects of this approach, referring for details to [25–28].

2. Indirect-exchange pairing in superconductors

The concept of indirect-exchange pairing, or exchange-mediated pairing, between conduction electrons via closed-shell (Wannier) “cores” is related to the well-known phenomenon of indirect exchange (“superexchange”) in magnetic insulators such as K_2NiF_4 , NiO , MnS , etc., in which unpaired electrons on neighboring paramagnetic cations interact via closed-shell anions (F^- , O^{2-} , S^{2-}) giving rise, at temperatures up to ≈ 200 K in some materials, to magnetic ordering of the electron spins in antiferromagnetic, ferromagnetic, or more complex spin patterns. When generalized to itinerant electrons such interactions can lead, in the s-wave channel, to Cooper-pair formation in specific cases [25] (in simple metals, closed-shell cation cores (e.g. Cs^+) can act as mediators).

In cuprates, the diamagnetic cores are closed-shell oxygen anions O^{2-} . Further generalization shows that in alkali-doped C_{60} , carbon-carbon double bonds mediate pair formation [29], whereas in organic superconductors of the (BEDT-TTF) type, sulfur or selenium atoms may fulfill this role [30].

We adopt the BCS formalism, with the specification that the off-diagonal scattering-matrix (configuration-interaction) elements V_{qk} are due to indirect-exchange, not to electron-phonon, coupling. In this formalism, the critical temperature T_c is obtained in the form [25–29]

$$T_c = \langle A\omega \rangle \exp\left(\frac{-1}{|W|}\right), \quad \text{for } W < 0, \quad (1)$$

where $\langle A\omega \rangle$ is a characteristic temperature for the indirect-exchange coupling, taken proportional to the Fermi energy of the conduction electrons. The quantity $|W|$ is the coupling strength, defined [25,26] as a function of V_{qk} (near the Fermi surface) and of the density-of-states in an effective-mass approximation (electron band mass m^*). For small Fermi vector k_F , we assume an isotropic conduction band; henceforth k_F will be used to denote $|k_F|$.

The formalism leading to an algebraic expression for the coupling W was presented in the original paper [25], to which we refer for details. To obtain numerical results we must introduce approximations for the wavefunctions of core and conduction electrons. Each core is represented by two, spin-paired, electrons on a simple Gaussian orbital with characteristic parameter α (the “larger” the core, the smaller is α). The wavefunction for a conduction electron is approximated by a “theta” function, i.e. a plane wave modulated by simple Gaussian functions at the sites of the cores, with characteristic parameter β . Thus β is a “localization” parameter determining the overlap with core (Wannier) wavefunctions. In the absence of cores $\beta = 0$, and the theta function is just a plane wave. This means that in a band formalism β is a continuous function of the core density ρ_c ; for dimensional reasons it follows that $\beta \propto \rho_c^{2/3}$.

The principal result of the analysis is that W is obtained as a function of α , β , and k_F ,

$$W = W(\alpha, \beta, k_F), \quad (2)$$

which can be evaluated for different values of the three parameters. We underline that W also contains the direct (Coulomb) interaction between the conduction electrons.

In the cuprate superconductors, α refers to the oxygen anion O^{2-} ; its value is 0.469 au^{-2} , directly taken over from an earlier analysis of superexchange in magnetic oxides (details are given in [27]). The original computations [25] were carried out taking Cs metal as a gauge system, to avoid the necessity of separately listing W values for each system considered. The value of α for O^{2-} , scaled to the atomic density of Cs, amounts to $\approx 0.20 \text{ au}^{-2}$.

To conclude this summary of previous results, it was found [26,27] that, at the maximum of T_c in the Tl_2 -cuprates with $N = 1, 2$ and 3 CuO_2 layers per molecular unit, $\langle A\omega \rangle \approx 200 \text{ K}$. The effective-mass ratio m^*/m_e (m_e is the mass of a free electron) amounts to 4.5–5 in the cuprates, in satisfactory agreement with experiment.

Values of W , as a function of β , for different k_F , and $\alpha = 0.20 \text{ au}^{-2}$, as well as for different α , at $k_F = 0.341 \text{ au}^{-1}$ (Cs metal), are plotted in [29–31]. Taking $\alpha = 0.20 \text{ au}^{-2}$, $k_F = 0.341 \text{ au}^{-1}$ as an example, it is found that $W < 0$ for $0.11 \leq \beta \leq 0.23 \text{ au}^{-2}$, i.e. superconductivity is possible only within these limits. Inside this region $|W|$ increases steeply between 0.11 and 0.17 au^{-2} , followed by a maximum (for one CuO_2 layer, and $m^* = m_e$) $|W| \approx 0.3$ at $\beta \approx 0.18 \text{ au}^{-2}$, and a steep decrease thereafter. For larger α the maximum in $|W|$ decreases and shifts to larger values of β . Beyond $\alpha \approx 0.35 \text{ au}^{-2}$ superconductivity has disappeared. Further, a rapid decrease of $|W|$ is found upon increasing k_F . This is due to a more rapid change in space of the plane-wave part $\exp(ik_F \cdot r)$ of the conduction-electron wavefunction *across* a core, resulting in steeply diminishing overlap and exchange integrals. It explains, for example, the steep decrease in T_c beyond optimum doping x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [28] (at very small k_F , $|W|$ first increases with k_F because the density-of-states is proportional to k_F).

3. Application to $\text{Hg}(N)$ -cuprates; comparison of ambient pressure properties with the $\text{Tl}_2(N)$ series

The indirect-exchange pairing mechanism will now be applied to superconductivity in the $\text{Hg}(N)$ high- T_c cuprates, for different numbers N of CuO_2 layers per molecular unit, and compared with the $\text{Tl}_2(N)$ series, at *ambient pressure*. The close similarity regarding crystal structures, unit-cell dimensions ($\frac{1}{2} C_N$ in the Tl_2 series compared with C_N in $\text{Hg}(N)$), as well as the observed maximum T_c for $N = 3$ in both families indicate that, in first approximation, superconductivity in the two series may be analyzed on the same basis. We thus ignore for the moment the markedly different high-pressure dependence of T_c , e.g. the fact that T_c of $\text{Tl}_2(N = 3)$ reaches a maximum of only 133 K (at $P = 4.2 \text{ GPa}$), whereas T_c for $\text{Hg}(N = 3)$ continues to increase considerably beyond 150 K at high pressure, in spite of the *close agreement* between their dT_c/dP values at $P = 0$ (1.7–1.8 K/GPa). The central task consists of evaluating the coupling $W(\alpha, \beta, k_F)$ for the two series, in which oxygen fulfills a *double role* [28]: as a hole dopant in the CuO_2 layers, contributing (indirectly) to k_F of the conduction electrons, and as a Cooper-pair mediator, reflected in the parameter β , proportional to $[\rho(\text{O}^{2-})]^{2/3}$. We concentrate on a comparison between β values for the two families as a function of the number N of CuO_2 layers per molecular unit, assuming that the effective mass of the carriers, and the density-of-states for the same N , may be taken the same between the two series.

A detailed analysis of the $\text{Tl}_2(N)$ series was given in an earlier paper [27]. Substantial agreement with the experimental T_c values of $\approx 85, 110$ and 125 K for $N = 1, 2$, and 3 , respectively, was there obtained with a *gauge* value $\beta = 0.15 \text{ au}^{-2}$ for $\text{Tl}_2(N = 1)$ and with $\langle A\omega \rangle = 180\text{--}220 \text{ K}$, counting $2N + 1$ oxygen anions per molecular unit. (details are given in [27]). Selecting a particular value for k_F is not essential, since the $W(\beta)$ -curves at different k_F have the same shape, and the β value at

maximum $|W|$ does not shift with k_F (see [29–31]). The nominal oxygen content in the $\text{Ti}_2(N)$ series is $2N + 4$ per molecular unit, from which 2 oxygens per $(\text{Ti}-\text{O})_2$ bilayer are to be subtracted. Considering only $2N + 1$ oxygens implies that the contribution to β from the two apical oxygens are weighed with a factor $\frac{1}{2}$. This may be rationalized by the fact that Cooper-pair formation takes place in, or near, the CuO_2 layers, and that the distance between an apical oxygen $\text{O}(2)$ and the nearest Cu is considerably larger than in-plane Cu–O separation ($\approx 1.93 \text{ \AA}$). In the $\text{Ti}_2(N)$ series, the Cu– $\text{O}(2)$ distance is (practically constant with N) $2.65 \text{ \AA}$. Since in the present mechanism Cooper-pair formation is an exchange effect, a strong dependence on distance between the oxygen considered and the nearest CuO_2 layer must be expected.

For the $\text{Hg}(N)$ series we proceed along parallel lines. The contribution from excess oxygen (δ), at the $\text{O}(3)$ sites in the Hg plane, to β is not considered: their fraction of the nominal oxygen content is small, and their distance to the nearest CuO_2 layer is large. The Cu-(apical) oxygen distance is $2.79 \text{ \AA}$ for $N = 1$ and $N = 2$, and $2.75 \text{ \AA}$ for $N = 3$ [16]. Consequently, a further reduction of the weight factor for apical oxygens may be expected. Detailed analysis, while varying this factor ($\leq \frac{1}{2}$), yields as the optimal result relative to the $\text{Ti}_2(N)$ series, for $N = 1, 2, 3$ and 4 CuO_2 layers, a weight factor of $5/16$ for each of the $\text{Hg}(N)$ apical oxygens. The gauge value of β for $\text{Ti}_2(N = 1)$, assumed to be 0.15 au^{-2} in [27], is slightly reduced to 0.145 au^{-2} ; this has only a minor effect on the β -values for this family. A factor of $\frac{1}{2}$ in $\text{Hg}(N)$ would result in $\beta(\text{Hg}, N = 1) = 0.164 \text{ au}^{-2}$ and $\beta(\text{Hg}, N = 3) = 0.204 \text{ au}^{-2}$. The latter value lies considerably beyond that for maximum $|W|$. On the other hand, selecting a factor $\frac{1}{4}$ yields $\beta(\text{Hg}, N = 1) = \beta(\text{Ti}_2, N = 1)$ suggesting equality of their T_c values, in disagreement with experiment.

The calculated β values are given below. Nominal oxygen content is assumed, with densities calculated from $(\text{Ti}_2) C_N/2 = 8.2 + 3.2N$, and $(\text{Hg}) C_N = 6.3 + 3.2N$ (experimental C_N values [1] for Ti_2 , [6] for Hg) yield only minor differences).

$N =$	1	2	3	4
$\text{Ti}_2(N)$	0.145 (gauge)	0.170	0.185	0.195
$\text{Hg}(N)$	0.150	0.175	0.190	0.200

These β values are plotted in Fig. 1 on the $W(\beta)$ -curve for $\alpha = 0.20 \text{ au}^{-2}$, $k_F = 0.341 \text{ au}^{-2}$.

It is seen from the figure that, just as with the $\text{Ti}_2(N)$ compounds, $|W|$ in $\text{Hg}(N)$ reaches a maximum at $N = 3$. With a slowly increasing density-of-states as a function of N [27], and in view of the steep decrease of $|W(\beta)|$ beyond its maximum (at $\beta = 0.184 \text{ au}^{-2}$), we anticipate a maximum T_c at $N = 3$ in the $\text{Hg}(N)$ series, in agreement with experiment [6].

A more detailed estimate of the difference $\Delta T_c(N)$ between the two series can be made for $N = 1$, in which case both β values lie on the steep part of the $|W(\beta)|$ -curve.

Fig. 1. Indirect-exchange coupling W as a function of the parameter β in the conduction-electron (theta) function, for $\alpha = 0.20 \text{ au}^{-2}$ (oxygen anion O^{2-}) and a length of the Fermi vector $k_F = 0.341 \text{ au}^{-1}$ (solid Cs as a gauge system). The circles refer to $\text{Tl}_2(N)$ systems with $N = 1, 2, 3$, and 4 (from left to right); triangles refer to $\text{Hg}(N)$ systems, again for $N = 1-4$ in the same order; $\beta = 0.145 \text{ au}^{-2}$ for $\text{Tl}_2(N = 1)$ is a gauge value. The calculations apply for nominal compositions.

Taking $\langle A\omega \rangle = 200 \text{ K}$ in both cases, a difference $\Delta T_c = 9$ (or 7) K between $T_c = 85 \text{ K}$ (or 87 K) for $\text{Tl}_2(N = 1)$ and 94 K for $\text{Hg}(N = 1)$ implies a difference $\Delta|W|$ of 1.32–1.17 (1.20) = 0.15 (0.12). To compare with computed $W(\beta)$ results, we must divide by $(m^*/m_e) \approx 5$ and obtain, with $d|W|/d\beta \approx 5.5 \text{ au}^2$, $0.15/5 \approx (5.5) \Delta\beta$, i.e. $\Delta\beta \approx 0.005 \text{ au}^{-2}$, with practically the same result for $\Delta T_c = 7 \text{ K}$. This value of $\Delta\beta$ agrees closely with that calculated from cell dimensions.

On the other hand, it is seen from Fig. 1 that for the $\text{Hg}(N = 2)$ and $\text{Hg}(N = 3)$ compounds the difference in $|W|$ with the Tl_2 series is too small to quantitatively explain the observed higher transition temperatures in the $\text{Hg}(N)$ series, i.e. $\Delta T_c \approx 10 \text{ K}$ ($N = 2$) and $\approx 6 \text{ K}$ ($N = 3$). For $N = 3$ we expect, from Fig. 1, $\Delta T_c \approx 0$, or a slightly lower T_c for the Hg-compound. Novikov and Freeman [20] obtain from band structure calculations an additional contribution to the DOS at the Fermi surface due to a Hg-(apical) oxygen derived band, of about 30% for $N = 2$, and 20% for $N = 3$ (no contribution for $N = 1$). In the Tl_2 compounds this extra

density-of-states is missing (the Tl6s–O2p band is found to be located below E_F for $N = 1, 2, 3$). Such contributions may well raise the critical temperatures for Hg($N = 2$) and Hg($N = 3$) to the values observed.

Summarizing the results of this section, we conclude that the indirect-exchange pairing mechanism provides a consistent interpretation of critical temperatures in the Hg(N) series, at *ambient pressure*. In addition, it accounts for similarities and differences with the closely related Tl₂(N) superconductors. The coupling strength $|W|$ decreases in both series for $N > 3$, and the calculated T_c for Hg($N = 1$) is higher than for Tl₂($N = 1$) by the correct amount. For the $N = 2$ and $N = 3$ members, agreement with experiment presupposes a somewhat larger density-of-states in the Hg(N) series, as suggested by band structure calculations [20].

4. Effect of pressure on T_c of the Hg(N) – and Tl₂(N) – series

In Sect. 3 it was found that application of the indirect-exchange pairing mechanism leads to substantial agreement with experimental transition temperatures, at ambient pressure, between the Hg(N) and Tl₂(N) series, provided that for Hg($N = 2$) and Hg($N = 3$) the density-of-states at E_F is somewhat enhanced due to a crossing Hg-(apical)O band [20]. We next analyze the effect of pressure on T_c for these families.

As was noted in the introduction, pressure experiments reveal *very considerable* differences between the two series. Specifically, Hg($N = 2$) and Hg($N = 3$) are reported [12,31] to reach T_c values of 154 K at $P \approx 29$ GPa and of 164 K at $P \approx 31$ GPa, respectively; T_c of the $N = 1$ member attains a maximum value of 118 K, at $P \approx 24$ GPa. *In contrast*, the critical temperature of Tl₂($N = 2$) only increases from 117 K at $P = 0$ to a maximum of ≈ 119 K at 1.9 GPa, with an initial slope 1.7 K/GPa [32]. For Tl₂($N = 3$), T_c is enhanced from 128.5 K at $P = 0$ to 133.0 K at $P = 4.2$ GPa, with a starting dT_c/dP of 1.75 K/GPa [11]. Very anomalous is the behavior of T_c under pressure for the $N = 1$ compound. A detailed experimental analysis for this system, i.e. Tl₂Ba₂CuO_{6+y}, was undertaken by Sieburger and Schilling [33], who compared pressure effects up to 0.6 GPa for different excess oxygen y . The critical temperature at $P = 0$ strongly depends on oxygen content (ranging from 90 K at $y = 0.10$ to 0 K at $y \geq 0.23$). These authors established that applying pressure at room temperature (method A) or at $T_c + 10$ K (method B) yields very different results. For example, dT_c/dP at $P = 0$ for $y = 0.18$ ($T_c = 36.0$ K) is -6.6 K/GPa (method A) and $+0.2$ K/GPa (method B).

4.1. Concepts and equations used

The following analysis of pressure effects on T_c is based in part on a recent paper [28] dealing, in particular, with the cuprates La_{2–x}Sr_xCuO₄ and (Yb,Ca)(Ba,Sr)₂Cu₃O_z for different doping levels x and z , respectively. In the indirect-exchange formalism, pressure (external, or “chemical”) affects directly the parameters

β and k_F in the coupling $W(\alpha, \beta, k_F)$. Explicitly, $\beta^{3/2}$ is proportional to the density of (“ β -active”) oxygen (anions O^{2-}), whereas k_F varies as $V^{-1/3}$ in the effective-mass approximation; V is the volume of the system. “Pressure-induced hole transfer” to the CuO_2 layers, a phenomenological concept in many qualitative discussions of pressure effects, is *not considered* in what follows.

To obtain algebraic expressions, we observed that the $W(\beta)$ curves for different k_F (cf. Fig. 1 of [29,30,34]) have the same shape, and that the β value at maximum $|W|$ does not shift with k_F . This implies that, *in the range of β of interest for superconductivity*, a separation of the variables β and k_F in W holds to good approximation. We write [28]

$$|W| = \frac{bk_F}{\alpha^{1/2}} f\left(\frac{bk_F}{\alpha^{1/2}}\right) g(\beta), \quad (3)$$

with b a materials constant for the cuprates; α is, as before, the Gaussian parameter for the diamagnetic unit (O^{2-}), whereas the function $g(\beta)$ also contains the effective mass m^* of the conduction electrons. The constant b implies a scaling of the length of the Fermi vector. The dimensionless parameter $k_F/\alpha^{1/2}$ is a characteristic quantity for the modulation of the conduction-electron wavefunction across a diamagnetic unit. For very small $k_F/\alpha^{1/2}$ this variation is minimal; with increasing k_F (filling of the conduction band) the modulation becomes stronger, resulting in a quenching of all overlap and exchange integrals, as remarked in Sect. 2. The factor k_F in W arises from the density-of-states.

In order not to complicate the notation we abbreviate $bk_F/\alpha^{1/2}$ by κ . Using $\langle A\omega \rangle = a\kappa^2$, it follows from (1) and (3) that

$$\frac{d \ln T_c}{d\kappa} = \frac{2}{\kappa} + \left(\frac{1}{|W|\kappa} \right) \left(1 + \kappa \frac{d \ln f}{d\kappa} \right). \quad (4)$$

To derive the expression for $d \ln T_c / dP$, we first determine $d \ln T_c / dV$ and then use $d \ln T_c / dP = -(V/B) d \ln T_c / dV$, with $B \equiv -V dP / dV$, the bulk modulus of the system. The result is [28]

$$\frac{d \ln T_c}{dP} = \left(\frac{1}{3B} \right) \left(2 + \frac{1}{|W|} \left(1 + \kappa \frac{d \ln f}{d\kappa} \right) + \frac{1}{|W|} \frac{2\beta}{g} \frac{dg}{d\beta} \right). \quad (5)$$

The equality (5) expresses that the effect of pressure on T_c is taken to be entirely due to a change of *volume* of the system, i.e. we exclude pressure-induced charge transfer to the CuO_2 layers. Nor do we consider anisotropic compression, and we neglect for the moment a possible change of weight factors (in determining the value of β) of the apical oxygens at high compression.

For doping at *constant* β , e.g. in $La_{2-x}Sr_xCuO_4$, or in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ [34], it is easily found that at maximum T_c , i.e. optimum doping x , the first and second

terms inside the brackets cancel each other. We then have (maximum T_c , constant β)

$$\frac{d \ln T_c}{dP} = \frac{1}{3B} \frac{2\beta}{W^2} \frac{d|W|}{d\beta}, \quad (6)$$

independent of the functional form of $f(\kappa)$.

Eq. (6) illustrates the role of oxygen as a Cooper-pair mediator: if dT_c/dP would be determined by k_F only, i.e. $g(\beta)$ is constant, then $dT_c/dP = 0$ at maximum T_c , negative thereafter. *No cuprate superconductor shows this behavior.*

As an example we calculate, from (6), the value of $d \ln T_c/dP$ at maximum $T_c = 40$ K for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Since the expression $(\beta/|W|)(d|W|/d\beta)$ is independent of κ (thus of k_F) and of m^*/m_e , as well as invariant with respect to density scaling, its value can be directly taken from the computed $W(\beta)$ curve (with $k_F = 0.341 \text{ au}^{-1}$, $m^* = m_e$, and the atomic density of solid Cs). For $\langle A\omega \rangle = 200$ K at maximum $T_c = 40$ K the $|W|$ value on the computed curve is $0.621/5 = 0.124$, corresponding with $\beta = 0.13 \text{ au}^{-2}$. One obtains, for a bulk modulus $B = 100$ GPa, and a slope $d|W|/d\beta \approx 5.5(m^*/m_e)$,

$$\frac{d \ln T_c}{dP} \approx \left(\frac{1}{300} \right) \left(\frac{2 \times 0.13}{0.621} \right) \left(\frac{5.5}{0.124} \right) = 6.2 \times 10^{-2} \text{ GPa}^{-1},$$

yielding $dT_c/dP \approx 2.5 \text{ K/GPa}$. The experimental value is 2–3 K/GPa, i.e. the indirect-exchange coupling reproduces the correct result for dT_c/dP of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. For more details we refer to [28].

To obtain numerical results in the general case, we must specify $f(\kappa)$. The computed curves suggest the simple form $f(\kappa) = \exp(-\kappa^2)$, expressing the calculated rapid decrease of $\kappa f(\kappa)$ for large k_F . Eq. [5] now reads

$$\frac{d \ln T_c}{dP} = \left(\frac{1}{3B} \right) \left(2 + \frac{1}{|W|} (1 - 2\kappa^2) + \frac{1}{|W|} \frac{2\beta}{g} \frac{dg}{d\beta} \right). \quad (7)$$

For the special case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the last term inside the parentheses is the dominant one, at ambient pressure, for all κ (i.e., all x), i.e. $d \ln T_c/dP > 0$ throughout the relevant doping range. Only at very large κ will $(1 - 2\kappa^2)$ be sufficiently negative to render $dT_c/dP < 0$. However, $|W|$ is then so small that superconductivity has all but disappeared.

From (7) we anticipate the form of $T_c(P)$ for increasing pressure: higher P implies larger κ and larger β , i.e. moving with β to the right on the $g(\beta)$ curve. Starting from a positive dT_c/dP at $P = 0$, a change of sign of this slope occurs, i.e. T_c decreases after a critical value of the pressure, depending on the system considered. Obviously, a sign change of dT_c/dP for hole-doped cuprates may be reached experimentally only if $\beta(P = 0)$ is not much smaller than its value at maximum $g(\beta)$, i.e. if $T_c(P = 0)$ is high on the scale of cuprate critical temperatures.

We turn to the effect on T_c of oxygen loading in the $\text{Hg}(N)$ and $\text{Tl}_2(N)$ series. Assuming theoretically that this can be carried out at constant volume, we distinguish between two limiting cases: (A) the added oxygen is incorporated in the lattice as

anions O^{2-} in the neighborhood of the CuO_2 layers (filling of vacancies or interstitials), and (B) the oxygen is stored as anions O^{2-} inside the Hg plane (increasing δ in $HgBa_2Ca_{N-1}Cu_NO_{2N+2+\delta}$), or inside the $(Tl-O)_2$ bilayers. In case (A), adding oxygen changes both the values of κ and β , whereas in (B) only κ is affected (hole doping); the density of “pair-mediating” oxygens remains the same in this case.

Combining the two possibilities we can write, denoting by ρ the oxygen density,

$$\left(\frac{d \ln T_c}{d\rho}\right)_V = \left(\frac{d \ln T_c}{d\kappa}\right)\left(\frac{d\kappa}{d\rho}\right)_V + \left(\frac{d \ln T_c}{d\beta}\right)\left(\frac{d\beta}{d\rho}\right). \quad (8)$$

On the right-hand side the subscript “V” in all derivatives except $d\kappa/d\rho$ is redundant. The expression for $d \ln T_c/d\kappa$ is given by (4), whereas $d \ln T_c/d\beta = (1/W^2)d|W|/d\beta$. In case (A), with added O^{2-} in the neighborhood of CuO_2 layers, $d\beta/d\rho = 2\beta/3\rho$, from $\beta \propto \rho^{2/3}$, whereas in case (B) $d\beta/d\rho = 0$.

The change in κ (i.e. k_F) upon oxygenation is, however, *not known*: the Fermi vector (length) of the conduction electrons is only indirectly related to the oxygen density. Oxygenation leads to an increase of holes in the CuO_2 layers which, in turn, increases k_F (as in $La_{2-x}Sr_xCuO_4$ with larger x). The precise relation between oxygen content and k_F is still an unsolved problem beyond the conjecture $d\kappa/d\rho > 0$.

Using (4) and taking, as before, $f(\kappa) = \exp(-\kappa^2)$, one obtains for case (A)

$$\left(\frac{d \ln T_c}{d\rho}\right)_V = \left(2 + \frac{1}{|W|}(1 - 2\kappa^2)\right)\left(\frac{d \ln \kappa}{d\rho}\right)_V + \left(\frac{2\beta}{3\rho W^2}\right)\left(\frac{d|W|}{d\beta}\right), \quad (9)$$

which expression is similar to (7) for $d \ln T_c/dP$. Note that in $d \ln T_c/dP$ the change in κ is a volume effect, with $\kappa \propto V^{-1/3}$.

4.2. Procedure used for evaluating $T_c(P)$

We now go over to the determination of critical temperatures $T_c(P)$ of the $Tl_2(N)$ and $Hg(N)$ cuprates under pressure, starting from given T_c values at ambient pressure $P = 0$. The dependence on P of the parameters $\kappa \equiv bk_F/\alpha^{1/2}$ and β is easily established; given their values κ_0, β_0 at $P = 0$, and noting that κ varies with volume as $V^{-1/3}$, β as $V^{-2/3}$ (i.e. we consider volume changes only), it follows that

$$\kappa(P) = \kappa_0 \exp\left(\frac{P}{3B}\right); \quad \beta(P) = \beta_0 \exp\left(\frac{2P}{3B}\right), \quad (10)$$

with $B \equiv -VdP/dV$ the bulk modulus of the system. Thus, from given κ_0, β_0 and B , the values of $\kappa(P)$ and $\beta(P)$ follow directly. However, a given $T_c(P = 0)$ does not determine κ_0 and β_0 ; in addition, with $\langle A\omega \rangle$ in (1) at $P = 0$ of the form $a\kappa_0^2$, the additional parameter a has to be known.

We can, nevertheless, in principle obtain κ_0, β_0 and a via a detour, through partial (heterovalent) substitution of the cations Ba^{2+} or Ca^{2+} , while leaving the oxygen density (ideally) the same. Partial substitution of Ba or Ca by an alkali atom leads to hole doping, i.e. (indirectly) to an increase of κ , as in $La_{2-x}Sr_xCuO_4$, whereas κ is

lowered by cations of e.g. charge $3+$ (such as Y^{3+} , La^{3+}). In this way, the maximal critical temperature (changing κ) $T_{c,m}$ can in principle be obtained.

Suppose that such an experiment can be carried out for a given thallium or mercury cuprate, leading to a value for $T_{c,m}$. In this system, (4) applies, resulting with $f(\kappa) = \exp(-\kappa^2)$ in

$$\kappa_m^2 = |W_m| + \frac{1}{2}. \quad (11)$$

Henceforth, the subscript “m” in W_m , κ_m etc. always implies “at $T_{c,m}$ ”. Taking $\langle A\omega \rangle$ at $T_{c,m}$ equal to 200 K [27], we determine $|W_m|$ from (1), then κ_m from (11), which also leads to the value of $g(\beta_0) = |W_m|/\kappa_m \exp(-\kappa_m^2)$ and to the proportionality factor a in $200 = a\kappa_m^2$. The oxygen density is assumed to remain unchanged under cation substitution, i.e. $\beta_m = \beta_0$.

Next we return to the original system with (given) T_c and substitute a and $g(\beta_0)$ into (1), which yields the κ_0 value belonging to T_c . Solutions for κ_0 occur in pairs: one with $\kappa_0 > \kappa_m$ in case the system at $P = 0$ is *overdoped with respect to κ* , and one with $\kappa_0 < \kappa_m$ if the system is *underdoped*. Both solutions must be considered in the calculation of $T_c(P)$, if the choice is not clear from the outset. To evaluate $T_c(P)$, the only remaining quantity to be determined is $g(\beta)$ for different β which is simply obtained as $g(\beta) = g(\beta_0) [W(\beta)/W(\beta_0)]$. Since all quantities are herewith determined as a function of pressure, the critical temperature $T_c(P)$, starting from $T_c(P = 0)$ and with known $T_{c,m}(P = 0)$ can be calculated.

In practice, the above cation-doping experiments aiming at a reliable measurement of $T_{c,m}$ is in most cases not be feasible. In the $Tl_2(N)$ and $Hg(N)$ cuprates, changing κ through oxygen loading and unloading of the $(Tl-O)_2$ bilayers, and increasing or decreasing the excess oxygen δ , respectively, without affecting the CuO_2 layers or the apical oxygens, is not yet within reach. In numerical calculations we choose $T_{c,m}$ equal to (maximum) T_c plus a variable small increment ($T_{c,m} \geq T_c$ irrespective of whether the system at T_c is under- or overdoped with respect to κ_m).

5. Numerical results

5.1. The systems $Hg(N = 1)$ and $Tl_2(N = 1)$ under pressure

The procedure developed in Sect. 4.2 is now applied to a numerical evaluation of $T_c(P)$ for the $Hg(N)$ and $Tl_2(N)$ cuprates, starting with $N = 1$, i.e. with $HgBa_2CuO_{4+\delta}$ and $Tl_2Ba_2CuO_{6+y}$. In the case of $Hg(N = 1)$ we take $T_c = 95$ K and vary $T_{c,m}$, the critical temperature at optimal κ , as $T_{c,m} = 100, 105$, and 110 K. With the temperature $\langle A\omega \rangle$ in (1) equal to 200 K at $T_{c,m}$ (throughout the two series), a choice of $T_{c,m}$ leads to values for W_m and κ_m , $g(\beta)$, and the factor a in $a\kappa_m^2 = 200$ K, as was explained in 4.2.

For the Gaussian parameter β in the conduction-electron wavefunction a value of 0.150 au^{-2} was determined (Sect. 3) relative to a gauge value $\beta = 0.145 \text{ au}^{-2}$ of the

compound $Tl_2(N = 1)$ at nominal composition. We allow a slight margin in β by considering also $\beta = 0.155 \text{ au}^{-2}$ (implying an increase of (active) oxygen density by about 5 percent, using $\rho \propto \beta^{3/2}$). Concerning the original system ($T_c = 95 \text{ K}$ at $P = 0$), κ_0 is determined from T_c and $g(\beta)$, both in an *underdoped* ($\kappa_0 < \kappa_m$) and an *overdoped* ($\kappa_0 > \kappa_m$) version, as outlined in 4.2. The dependence on pressure of κ and β is given by (10). The bulk moduli of the $Hg(N)$ series have recently been carefully determined by Hunter et al. [16] using neutron powder diffraction techniques resulting in $B = 70$ ($N = 1$), 84 ($N = 2$) and 93 GPa ($N = 3$).

In Table 1 we list the results of the calculation for the maximum T_c obtained, the pressure P at that maximum, and the gradient dT_c/dP at $P = 0$, with $\beta = 0.150$ and 0.155 au^{-2} , at each chosen value of $T_{c,m}$ (100, 105 and 110 K).

Comparing the tabulated results with the experimental values maximum $T_c \approx 118 \text{ K}$, $P(\text{at maximum } T_c) \approx 24 \text{ GPa}$ [12,31] and $dT_c/dP = 1.72 \pm 0.05 \text{ K/GPa}$ [14], it is seen that *quantitative agreement* is obtained with $\beta = 0.155 \text{ au}^{-2}$, $T_{c,m} = 105 \text{ K}$, and *underdoped* $Hg(N = 1)$. A detailed plot of $T_c(P)$, up to 30 GPa, using these values is presented in Fig. 2, for both ($\kappa -$) underdoped and overdoped Hg ($N = 1$).

The most striking characteristic of the $T_c(P)$ curve for the underdoped system is the extensive near-linearity with increasing pressure. Whereas in the overdoped case a maximum T_c (105.8 K) is already reached at 11 GPa, the value of dT_c/dP for the underdoped system has only decreased from 1.7 to 1.2 K/GPa at that pressure, with the two curves starting at $P = 0$ from the same slope of 1.7 K/GPa (which is not generally the case). We also note that the contribution to dT_c/dP arising from the pre-exponential term $\langle A\omega \rangle$ in the equation for T_c , equal to $2T_c/3B$ from (7), has the

Table 1
Results for maximum T_c under pressure for $Hg(N = 1)$, the associated pressure and the initial slope dT_c/dP , listed for the values 0.150 au^{-2} and 0.155 au^{-2} of the parameter β in the conduction-electron (theta) function, at three chosen values of the critical temperature $T_{c,m}$ at optimum $\kappa (= bk_F/x^{1/2})$. Both under- and overdoped (with respect to κ_m) systems are considered. Agreement with experiment [12,14,31] is quantitative for $T_{c,m} = 105 \text{ K}$ and $\beta = 0.155 \text{ au}^{-2}$.

$T_{c,m}$ (K)	β (au^{-2})	$T_c(\text{max})$ (K)		$P(\text{at } T_c(\text{max}))$ (GPa)		dT_c/dP (K/GPa)	
		under	over	under	over	under	over
100	0.150	125.2	116.6	23–24	16	2.1	2.3
	0.155	117.5	109	20	13	1.8	1.9
105	0.150	125.1	112.5	25–26	14–15	1.9	2.2
	0.155	117.9	105.8	21–22	11	1.7	1.7
110	0.150	124.8	109	26–27	12–13	1.7	2.0
	0.155	118.1	103.1	23	9–10	1.6	1.5
experiment:		≈ 118	[12,31]	≈ 24	[12,31]	1.72 ± 0.05	[14]

Fig. 2. Calculated critical temperatures $T_c(P)$ for under-(un) and overdoped (ov) $\text{Hg}(N=1)$, with pressure in the range 0–30 GPa. The system is under- or overdoped with respect to the optimal value of $\kappa = \hbar k_F / \alpha^{1/2}$ (see text). The chosen value for β is 0.155 au^{-2} .

value 0.9 K/GPa at $P = 0$. Thus, the component of dT_c/dP from the coupling strength $|W|$ accounts for practically half the initial dT_c/dP .

We now consider $\text{Ti}_2(N=1)$, i.e. $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+y}$ under pressure, showing a much more complex behavior than is the case with $\text{Hg}(N=1)$. The results of the analysis will be confronted with those of a detailed experimental study of this system by Sieburger and Schilling [33] for values of y from 0.10 to 0.23, and pressures to 0.6 GPa. As mentioned in Sect. 4, T_c at $P = 0$ decreases from 90 K at $y = 0.10$ to 0 K at $y = 0.23$.

The effect of pressure on T_c is strongly anomalous; applying pressure at room temperature and then cooling results in a *negative* dT_c/dP , between -0.5 ($T_c = 13$ K) and -6.6 K/GPa ($T_c = 36$ K) whereas at maximum $T_c (= 90$ K) the slope is positive ($+0.9$ K/GPa). On the other hand, if pressure is changed at a temperature 10 K above $T_c(P)$ of the sample considered, then dT_c/dP is invariably much less negative, or *positive*. For example, with $y = 0.18$ ($T_c = 36$ K at $P = 0$), dT_c/dP in the first type of experiment is -6.6 ± 0.2 K/GPa, in the second experiment $+0.2 \pm 0.4$ K/GPa, whereas for $T_c = 90$ K, $dT_c/dP = +1.5 \pm 0.4$ K/GPa.

We assume that these anomalies are associated with the dynamics of interstitial oxygen at room temperature. Further evidence is provided by a recent observation by Schirber et al. [35] who succeeded in reducing the excess oxygen in $\text{Ti}_2(N=1)$ to a minimum value using Ar (at 0.3 kbar, 850°C for 3 h) to arrest the loss of Ti. The value of dT_c/dP was found to be about $+2$ K/GPa, irrespective of the temperature at which pressure is applied. Expecting that such effects are not (or much less) important in $\text{Hg}(N=1)$, results of the following analysis are compared with those of experiments [33,36] in which pressure was changed *at low temperatures*.

Calculations of $T_c(P)$ were carried out for $T_c(P=0) = 90$ K (max), 36 K and 58 K, corresponding with $y = 0.10$, 0.18, and 0.15, respectively, and a bulk modulus $B = 82$ GPa as listed by Hunter et al. [16]. Since experimental values (pressure changes at $T_c + 10$ K) are not available beyond $P = 0.6$ GPa, we compare calculated and experimental values of the slope dT_c/dP at $P = 0$ and of $T_c(P)$ in the range 0–1 GPa. For the maximum $T_c(P=0)$ of 90 K, calculations were also carried out up to 30 GPa, with $T_{cm} = 95$, 100, and 105 K. For the values of β we chose 0.150 and 0.155 au^{-2} , i.e. the same as with $\text{Hg}(N=1)$.

In the following Fig. 3 results are given at $T_c = 90$ K ($P=0$), $T_{cm} = 105$ K, $\beta = 0.155 \text{ au}^{-2}$, $B = 82$ GPa, for pressures ranging from 0 to 30 GPa. The calculated dT_c/dP is 1.4 K/GPa (for both the under- and overdoped systems), in agreement with the experimental value of 1.5 ± 0.4 K/GPa [33].

A similar behavior of $T_c(P)$ is observed as with $\text{Hg}(N=1)$ (see Fig. 2). Although the initial slopes are even the same for $\text{Ti}_2(N=1)$, at high pressures the curves behave quite differently for under- and overdoped systems, as was found with the Hg-compound. In the underdoped case a maximum T_c of 113 K, at $P = 26\text{--}28$ GPa, is reached, whereas for overdoped $\text{Ti}_2(N=1)$, $T_c(\text{max}) = 99$ K, at $P = 12$ GPa. The corresponding dT_c/dP at $P = 0$ for $\beta = 0.150 \text{ au}^{-2}$ are 1.8 (over-) and 1.7 (underdoped) K/GPa. Lowering T_{cm} raises dT_c/dP somewhat, from 1.4 K/GPa at $T_{cm} = 105$ K to 1.7(1.6) K/GPa at $T_{cm} = 95$ K (1.6 refers to the underdoped case) with $\beta = 0.155 \text{ au}^{-2}$, and similarly for $\beta = 0.150 \text{ au}^{-2}$.

Of particular interest is a comparison between experimental and calculated values of the slope at $P = 0$ for the systems with $T_c = 36$ K ($y = 0.18$ in $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+y}$) and 58 K ($y = 0.15$). Sieburger and Schilling [33] measured for these systems

Fig. 3. Calculated critical temperatures $T_c(P)$ for under-(un) and overdoped (ov) $\text{Ti}_2(N=1)$ with pressure up to 30 GPa, assumed to be applied at low temperatures. The value chosen for β is 0.155 au^{-2} .

$dT_c/dP = 0.2 \pm 0.4$ K/GPa at $T_c = 36$ K, and 0.6 ± 0.4 K/GPa at $T_c = 58$ K, i.e. much lower values than at $T_c = 90$ K ($P = 0$); for $T_c = 36$ K the critical temperature changes *hardly at all* with pressure in the range 0–0.6 GPa. In a more recent publication, Takahashi et al. [36] analyzed the effect of pressure on T_c for a sample with $T_c = 48$ K at $P = 0$, applying pressure (0–0.6 GPa) both at room temperature and at 55 K. The results are very similar to those of Sieburger and Schilling [33]. Results of the calculations are listed in Table 2, for $T_{c,m} = 95, 100$, and 105 K, $\beta = 0.150 \text{ au}^{-2}$ and 0.155 au^{-2} . For completeness, values of dT_c/dP at 90 K are included in the table, in this case for both over- and underdoped systems.

As with the Hg($N = 1$) superconductor, we find *quantitative* agreement with experiment for $\beta = 0.155 \text{ au}^{-2}$, and a critical temperature at optimum doping $T_{c,m} = 105$ K. With $y = 0.18$ ($T_c = 36$ K), T_c is *indeed* calculated to remain practically unchanged with pressure in the range 0–1 GPa; at 0.6 GPa, the highest experimental pressure [33], the calculated ΔT_c is +0.1 K. We note (Table 2) that also with $T_{c,m} = 95$ K and 100 K the value obtained for dT_c/dP at $T_c = 36$ K is lower than the upper experimental limit (0.5 and 0.3 against 0.6 K/GPa).

The closest agreement with experiment for Hg($N = 1$) and $\text{Ti}_2(N = 1)$ is here obtained for the same value $\beta = 0.155 \text{ au}^{-2}$, whereas in Sect. 3 the value of β for the Hg-compound was 0.150 au^{-2} relative to a gauge value of 0.145 au^{-2} for $\text{Ti}_2(N = 1)$. In fact, with the highest $T_c = 90$ K of the Tl-compound, also $\beta = 0.150 \text{ au}^{-2}$ for $T_{c,m} = 105$ K yields excellent agreement with the experimental dT_c/dP (calculated 1.8 for over-, 1.5 K/GPa for underdoped system; experimental 1.5 ± 0.4 K/GPa). On the other hand, with the 36 K, 48 K and 58 K samples (larger values of y) assuming

Table 2

Values of the initial slope dT_c/dP of $T_c(P)$ for the system $\text{Ti}_2(N = 1)$ at four critical temperatures (different excess oxygen contents), choosing three values for the critical temperatures $T_{c,m}$ at optimum $\kappa (= bk_F/\alpha^{1/2})$, and two values 0.15 au^{-2} and 0.155 au^{-2} for the β parameter. The results are compared with experimental data by Sieburger and Schilling [33] and by Takahashi et al. [36] with pressure applied (or changed) at $T_c + 10$ K.

$T_{c,m}$ (K)	β (au^{-2})	dT_c/dP (K/GPa)				
		$T_c = 36$ K	$T_c = 48$ K	$T_c = 58$ K	$T_c = 90$ K	
					over	under
95	0.150	0.8	1.1	1.4	2.0	1.8
	0.155	0.5	0.7	1.0	1.7	1.6
100	0.150	0.7	1.0	1.2	1.9	1.6
	0.155	0.3	0.6	0.8	1.5	1.5
105	0.150	0.5	0.8	1.1	1.8	1.5
	0.155	0.2	0.5	0.7	1.4	1.4
experiment		0.2 ± 0.4 [33]	0.4 ± 0.2 [36]	0.6 ± 0.4 [33]	1.5 ± 0.4 [33]	

$\beta = 0.150 \text{ au}^{-2}$ leads to much less satisfactory agreement with experiment (Table 2). This indicates that oxygen loading results in some incorporation in the bulk system, not exclusively in the $(\text{TI-O})_2$ bilayers. Further evidence to this effect can be deduced from the observation [33] that, starting from $y = 0.10$, oxygen (over) loading causes T_c to decrease *monotonically*. If all excess oxygen would be stored interstitially, then T_c should be expected to first increase with y until $T_{c_m} \approx 105 \text{ K}$ before falling off at larger y .

From the results for $\text{Hg}(N = 1)$ and $\text{TI}_2(N = 1)$ hitherto obtained, we conclude that the indirect-exchange pairing formalism provides detailed quantitative agreement with experiment regarding the effect of pressure on critical temperatures. These results are summarized in Table 1 and Fig. 2 for $\text{Hg}(N = 1)$, and in Table 2, Fig. 3 for $\text{TI}_2(N = 1)$. For the latter compound the comparison refers to experiments in which pressure is applied (or changed) *at low temperatures*, with $P = 0.6 \text{ GPa}$ as experimental limit [33,36].

The anomalous behavior of $T_c(P)$ for $\text{TI}_2(N = 1)$ with pressure applied at *ambient* temperature remains to be clarified. As mentioned before, dT_c/dP here varies between the large negative value of -6.6 K/GPa at $T_c = 36 \text{ K}$ (excess oxygen $y = 0.18$) to $+0.9 \text{ K/GPa}$ at $T_c = 90 \text{ K}$ ($y = 0.10$), and $+2 \text{ K/GPa}$ at 93 K ($y \approx 0$); the latter value holds irrespective of the temperature at which pressure is applied. Similar differences, though not as prominent as with $\text{TI}_2(N = 1)$, were observed by Schirber et al. [37] for dT_c/dP of “superoxygenated” $\text{La}_2\text{CuO}_{4+x}$ synthesized using either high oxygen pressure or through electrochemical oxygen loading. The pressure dependence of T_c was measured both at ambient temperature and below 60 K . The differences in values of dT_c/dP (smaller positive, or even negative, for pressure changed at ambient temperature) were assumed to result from reversible pressure-induced movement of excess oxygens stored in the LaO layers [37]; their mobility is quenched at low temperatures. Takahashi et al. [36] conjecture that with $\text{TI}_2(N = 1)$ there exists a relation between dT_c/dP and the strongly temperature-dependent, pressure-induced, rearrangement of interstitial oxygens in the $(\text{TI-O})_2$ bilayers. Such oxygen *orderings*, quenched at low temperatures, might strongly affect the superconducting state.

In the framework of the present formalism we propose the following solution to this problem. The expression (7) for $d \ln T_c / dP$ can be rewritten in the more general form

$$\frac{d \ln T_c}{dP} = \left(\frac{1}{3B} \right) \left(2 + \frac{1}{|W|} (1 - 2\kappa^2) \right) + \frac{1}{|W|} \frac{d \ln g}{d\beta} \frac{d\beta}{dP}, \quad (7')$$

which is identical with (7) for $d\beta/dP = 2\beta/3B$, as applied thus far. Separating out $d\beta/dP$, one has

$$\frac{d\beta}{dP} = \left[\frac{d \ln T_c}{dP} - \frac{1}{3B} \left(2 + \frac{1}{|W|} (1 - 2\kappa^2) \right) \right] / \left(\frac{1}{|W|} \frac{d \ln g}{d\beta} \right). \quad (12)$$

We now suppose that at ambient temperature, due to mobility of interstitial oxygen ions and to some pressure-induced diffusion from the $(\text{TI-O})_2$ bilayers into the bulk, the relation $d\beta/dP = 2\beta/3B$ *no longer* holds. Instead, mobile oxygen anions in the bulk, acting as Cooper pair mediators, *perturb* the conduction-electron wavefunction

(modulated at the oxygen sites) in oxygen overloaded system such as $\text{Ti}_2(N = 1)$). This perturbation leads to a relation $d\beta/dP < 2\beta/3B$, possibly even changing sign. If, on the other hand, pressure is applied at low temperatures, then the pressure-induced diffusion is quenched, and the relation $d\beta/dP = 2\beta/3B$ does hold.

We now investigate whether or not (12) is compatible with the *experimental* values of $d \ln T_c/dP$ at 36, 58, and 90 K [33], while imposing the following *a priori* conditions: (i) $d\beta/dP$ must be smaller than $2\beta/3B = +1.22 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$ in all three cases; (ii) $d\beta/dP$ must decrease with increasing excess oxygen content. Experimentally $d \ln T_c/dP$ is -18.3×10^{-2} (36 K), -11.0×10^{-2} (58 K) and $+1.0 \times 10^{-2}$ (90 K), in units GPa^{-1} . The values of κ and $|W|$ were already determined, whereas $d \ln g/d\beta$ is directly obtained from the computed $W(\beta)$ curve and is equal to 23.79 au^2 for the systems considered. The results for $|W|$ and κ , and for $d\beta/dP$ applying (12), are given in the following Table 3, with $\beta = 0.15 \text{ au}^{-2}$, $\langle A\omega \rangle = 200 \text{ K}$ at $T_{c,m} = 95 \text{ K}$, $B = 82 \text{ GPa}$. The systems at 36 K and 58 K are considered overdoped with respect to κ ; for $T_c = 90 \text{ K}$ we present values for both over- and underdoped cases.

From Table 3 it is seen that the conditions (i) and (ii) are fully satisfied. The relative changes $\Delta\beta/\beta$ per GPa, though quite small (-1.7% , -1.4% and $+0.44\%$ at $T_c = 36, 58$, and 90 K , respectively), *drastically* change dT_c/dP relative to measurements with pressure changes at low temperatures; this effect is due to the large value (23.79 au^2) of the term $d \ln g/d\beta$ in (7'). We interpret the above results as providing strong support for validity of the proposed explanation for the anomalous dT_c/dP values of $\text{Ti}_2(N = 1)$, arising from the effect on β by pressured-induced diffusion of interstitial oxygen anions.

5.2. The systems $\text{Hg}(N = 2,3)$ and $\text{Ti}_2(N = 2,3)$ under pressure

Next we analyze the development of critical temperatures with pressure for Hg ($N = 2$) (i.e. $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$) and Hg ($N = 3$) ($\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$), in comparison with $\text{Ti}_2(N = 2)$ (i.e. $\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$) and $\text{Ti}_2(N = 3)$ ($\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$). As was noted before, the differences between the two series become very pronounced for

Table 3

Calculated values for the slope $d\beta/dP$ of the parameter β , under pressure applied at *ambient* temperature, for $\text{Ti}_2(N = 1)$, at critical temperatures 36, 58, and 90 K, using the experimental results for $d \ln T_c/dP$ [33] (see text). Except with $T_c = 90 \text{ K}$, the systems are considered overdoped with respect to κ_m . A value of 0.15 au^{-2} is used for the β parameter. A negative $d\beta/dP$ implies that the system “resists” further oxygen overloading (through pressure-induced diffusion of oxygen anions from the $(\text{Ti}-\text{O})_2$ bilayers).

T_c (K)	$d \ln T_c/dP$ ($10^{-2}/\text{GPa}$) ref. [33]	$ W $		$ \kappa $		$d\beta/dP$ ($10^{-2} \text{ au}^{-2}/\text{GPa}$)	
		over	under	over	under	over	under
36	-18.3	0.438	—	1.802	—	-0.26	—
58	-11.0	0.593	—	1.689	—	-0.21	—
90	$+1.0$	1.022	1.736	1.485	1.215	$+0.066$	$+0.047$

more than one CuO_2 layer per molecular unit, especially for pressures beyond a few GPa. Whereas $\text{Hg}(N = 2)$ reaches a maximum T_c of 154 K at $P \approx 29$ GPa, and T_c of the $N = 3$ compound even attains 164 K at $P \approx 31$ GPa [12,31], the $\text{Tl}_2(N = 2)$ system increases its T_c from 117 K at $P = 0$ to a mere maximum of ≈ 119 K at $P = 1.9$ GPa [32], and the critical temperature of $\text{Tl}_2(N = 3)$ is raised under pressure from 128.5 K at $P = 0$ to only 133.0 K at $P = 4.2$ GPa [11]. On first sight, therefore, correlations between the two series cease to exist. It should be noted, however, that in experiments with $\text{Tl}_2(N = 2,3)$ pressure is invariably applied, or changed, at *ambient* temperature, so that anomalous behavior must be expected in view of the results of $\text{Tl}_2(N = 1)$ obtained in Section 5.1.

5.2.1. $\text{Hg}(N = 2)$

We first discuss the $N = 2$ system. Besides the highest T_c of 154 K reported by Gao et al. [12,31], Kosuge et al. [38], in a very recent analysis, applying quasi-hydrostatic pressure up to 8 GPa, measured an onset T_c of 144 K and a midpoint T_c of 140 K, without reaching saturation.

Calculations were carried out for $T_c = 127$ K, $T_{c,m} = 127 + 5 = 132$ K, $B = 84$ GPa, and for two β values: $\beta = 0.175 \text{ au}^{-2}$ for *nominal* composition, as determined in Section 3, and for $\beta = 0.15 \text{ au}^{-2}$, anticipating that in oxygen-deficient samples (not necessarily underdoped with respect to κ_m) the two CuO_2 layers may be “decoupled” with regard to superconductivity of the system. (A closer analysis will be given below.) The results, for both under- and overdoped cases, are presented in Fig. 4. The different curves are marked 0.175(ov), 0.175(un), 0.15(ov) and 0.15(un), respectively, with ‘ov’ = overdoped, ‘un’ = underdoped.

From the figure it is concluded that the results for $\beta = 0.175 \text{ au}^{-2}$ differ even *qualitatively* from the experimental data. Whereas for overdoped $\text{Hg}(N = 2)$, $T_c(P)$ continuously decreases with pressure, in the underdoped case T_c first increases to a maximum of 131.2 K at 10 GPa, then falls to 80 K at 30 GPa. The initial value of dT_c/dP is here 0.7 K/GPa.

However, with $\beta = 0.15 \text{ au}^{-2}$ (decoupled layers) the outcome for an underdoped system is in *striking* agreement with experiment: dT_c/dP at $P = 0$ is twice as high (1.5 K/GPa) as with $\beta = 0.175 \text{ au}^{-2}$ (0.7 K/GPa), though somewhat lower than the experimental value of 1.80 ± 0.06 K/GPa [13]. The maximum T_c is 153 K (exp. 154 K [12,31]) at a calculated pressure of 28 GPa (exp. 29 GPa [12,31]). For a pressure of 8 GPa, T_c is calculated to be 138 K, in excellent agreement with Kosuge et al. [38] who measured 140 K as (midpoint) T_c at that pressure. If we choose $T_{c,m} = T_c + 1 = 128$ K, then $dT_c/dP = 1.6$ K/GPa at $P = 0$; $T_{c,\text{max}} = 150.6$ K at $P = 24\text{--}25$ GPa. For an overdoped system and $\beta = 0.15 \text{ au}^{-2}$ we obtain $T_{c,\text{max}} = 139.4$ K at $P = 15\text{--}16$ GPa ($T_{c,m} = T_c + 5$ K), definitely to be ruled out, as expected.

We return to the surprising observation by Chen et al. [24] of a *break* in the $T_c(P)$ curve of $\text{Hg}(N = 2)$ for an oxygen annealed sample ($T_c = 117$ K) at $P = 0.4$ GPa; at lower oxygen content ($T_c = 111$ K) the break is *not* observed. On the basis of the

Fig. 4. Calculated critical temperatures $T_c(P)$ for under-(un) and overdoped (ov) $\text{Hg}(N=2)$, with pressure up to 30 GPa, for $\beta = 0.15 \text{ au}^{-2}$ (upper two curves) and $\beta = 0.175 \text{ au}^{-2}$ (lower two curves). The two values of β refer to a '2D' and '3D' system, respectively. The calculated maximum T_c amounts to 153 K (exp. 154 K) at a pressure of 28 GPa (exp. 29 GPa). Exp. values from [12,31].

results obtained with $\beta = 0.15 \text{ au}^{-2}$ and 0.175 au^{-2} we conjecture that this break implies a transition from a 2D ($P < 0.4 \text{ GPa}$) to a 3D ($P > 0.4 \text{ GPa}$) behavior, accompanied by an increase in β from 0.15 au^{-2} (2D) to 0.175 au^{-2} for a 3D-system (Sect. 3). For lower oxygen content ($T_c = 111 \text{ K}$) the system remains 2D under the pressure applied (up to 1.8 GPa). The above numerical results show that such a transition indeed results in reducing dT_c/dP by a factor of two, as Chen et al. observe. Since T_c is continuous at the breakpoint, a van Hove singularity is excluded as the cause of the phenomenon, as Chen et al. [24] remark. We suppose that also k_F remains the same, implying that both the coupling strength $|W|$ and the value of $g(\beta)$ in $|W| = \kappa f(\kappa)g(\beta)$ are unaffected at the transition. The value of β increases discontinuously from (2D) $\beta = 0.15 \text{ au}^{-2}$ to (3D) $\beta = 0.175 \text{ au}^{-2}$, so that there must be a discontinuity in the density-of-states, to which $g(\beta)$ is proportional, cancelling the effect of the change in β .

For other cuprates, a 2D–3D transition with increasing oxygen content has also been found. For example, Forro et al. [39] measure a metallic out-of-plane (normal-state) electrical resistivity for $\text{YBa}_2\text{Cu}_3\text{O}_x$ with the highest oxygen content ($x = 6.93$). Further, Xiang et al. [40] observe a sharp decrease of c -axis resistivity for iodine-intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ compared with the pristine system. This might be expected supposing that inserting iodine within the $(\text{Bi-O})_2$ bilayers leads to diffusion of oxygen anions from these bilayers towards the CuO_2 layers [34].

5.2.2. $Hg(N = 3)$

Development of the critical temperature with pressure for this compound has attracted the greatest interest in view of the highest T_c of 164 K reported by Gao et al. [12,31] at a pressure of 31 GPa, after an earlier result [8] by the same group of 153 K at 15 GPa. Nuñez-Regueiro et al. [41] reached an (onset) T_c of 157 K (midpoint 150 K) at 23.5 GPa, without saturation, whereas Ihara et al. [42] obtained a highest (onset) T_c of 156 K at 25 GPa. Finally, Takahashi et al. [43] reported a T_c , without specification, of 150 K at 11 GPa. The measured values of dT_c/dP at $P = 0$ vary from 1 to 2 K/GPa between the different experiments. Results at the highest pressures, determined electrically, invariably show a long non-zero resistivity tail below the transition, attributed to various causes such as defects introduced during thinning of the samples (by sandpaper in air), microcracks caused by using a solid pressure medium, or to pressure inhomogeneity across the anvil in these quasi-hydrostatic pressure techniques. In addition, the transition becomes broad, with a typical value for (onset) T_c -minus-(midpoint) T_c of 7–10 degrees, which complicates a more accurate determination of T_c .

We have carried out $T_c(P)$ calculations using $\beta = 0.15 \text{ au}^{-2}$ and $\beta = 0.19 \text{ au}^{-2}$. The latter value refers (Sect. 3) to nominal composition and a 3D system, whereas $\beta = 0.15 \text{ au}^{-2}$ applies for shielded (decoupled) CuO_2 layers similar to the case of 2D $Hg(N = 2)$. Further, $T_c = 134 \text{ K}$ and $T_{cm} = T_c + 5 \text{ K}$ as well as $T_c + 1 \text{ K}$. The bulk modulus of this system is 93 GPa [16]. In the following Fig. 5 results are presented for $T_{cm} = T_c + 5 = 139 \text{ K}$, in both over-(marked 'ov') and underdoped ('un') cases, with

Fig. 5. Same as in Fig. 4, now for $Hg(N = 3)$, with '2D' ($\beta = 0.15 \text{ au}^{-2}$, upper two curves) and '3D' ($\beta = 0.19 \text{ au}^{-2}$, lower two curves) systems. The calculated maximum T_c amounts to 158.6 K (exp. $\approx 164 \text{ K}$) at a pressure of 30–31 GPa (exp. 31 GPa). Exp. values from [12,31].

$\beta = 0.15 \text{ au}^{-2}$ (upper two curves) and $\beta = 0.19 \text{ au}^{-2}$ (lower two curves); the pressure range is 0–30 GPa.

Considering first $\beta = 0.19 \text{ au}^{-2}$ (“3D” system), it is seen that the results *strongly* deviate from the experimental data. Whereas in the overdoped system T_c decreases from the beginning, underdoped $\text{Hg}(N = 3)$ shows a very slight maximum $T_c = 134.3 \text{ K}$ at $P = 2\text{--}3 \text{ GPa}$. On the other hand, for $\beta = 0.15 \text{ au}^{-2}$ (“2D” system), T_c rises (underdoped) to a maximum of 158.6 K at $P = 30\text{--}31 \text{ GPa}$, in substantial agreement with experiment ([12,31] $T_c = 164 \text{ K}$ at $P = 31 \text{ GPa}$). The initial dT_c/dP is 1.3 K/GPa , within experimental limits of $1\text{--}2 \text{ K/GPa}$. Further, the calculated T_c at 23.5 GPa amounts to 156.6 K , compared with 157 K as found by Nuñez-Regueiro et al. [41], whereas for a pressure of 25 GPa the calculated T_c is 157.3 K , in excellent agreement with 156 K at that pressure determined by Ihara et al. [42]. Our calculated T_c at 15 GPa is 150.4 K , against 153 K (with a main transition at 147 K) measured by Chu et al. [8]. For an overdoped system the maximum T_c is 143.8 K , at $P = 15\text{--}16 \text{ GPa}$. The corresponding values for $T_{c,m} = 135 \text{ K}$ are (underdoped) $T_{c,\text{max}} = 155.7 \text{ K}$ at $P = 26\text{--}27 \text{ GPa}$, (overdoped) $T_{c,\text{max}} = 149.2 \text{ K}$ at $P = 19\text{--}21 \text{ GPa}$.

We conclude that the indirect-exchange pairing formalism yields *quantitative* agreement with experiment also for $\text{Hg}(N = 3)$, on the basis of a 2D interpretation of superconductivity, assuming that $\text{Hg}(N = 3)$ is slightly underdoped with respect to κ_m .

We finally compare experimental values of dT_c/dP measured by Klehe et al. [13] on samples of $\text{Hg}(N = 2)$ and $\text{Hg}(N = 3)$ annealed in argon gas at 500°C for 6 h, leading to a lowering of T_c to 94 K in both cases, with our calculated results. These authors find $dT_c/dP = +1.7 \text{ K/GPa}$ for $N = 2$, $+1.2 \text{ K/GPa}$ for $N = 3$ (presumably with an accuracy of $\pm 0.06 \text{ K/GPa}$). They compare these results with a model proposed by Neumeier and Zimmermann [44] in which dT_c/dP is separated into a part arising from “pressure-induced charge transfer” and an “intrinsic” contribution from all other sources. Klehe et al. conclude that this model would predict dT_c/dP at 94 K to be *larger* than at 127 K for $N = 2$ ($\approx 1.80 \text{ K/GPa}$) and *larger* than at 134 K for $N = 3$ ($\approx 1.71 \text{ K/GPa}$), in disagreement with their results.

With $T_c = 94 \text{ K}$ ($N = 2$ and 3), $T_{c,m} = 132 \text{ K}$ ($N = 2$) and 139 K ($N = 3$), $\beta = 0.15 \text{ au}^{-2}$ in both cases, we obtain $dT_c/dP = +1.0 \text{ K/GPa}$ for $N = 2$, $+0.8 \text{ K/GPa}$ for $N = 3$, indeed *lower* than for $T_c = 127 \text{ K}$ (calculated $+1.5 \text{ K/GPa}$) and for $T_c = 134 \text{ K}$ (calculated $+1.3 \text{ K/GPa}$), in (qualitative) agreement with experiment. We note that both the dT_c/dP values for argon annealed and original (highest T_c) samples are lower for $N = 3$ than for $N = 2$, as found experimentally.

5.2.3. $\text{Ti}_2(N = 2)$

For the second member of the Ti_2 series, i.e. $\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$, we take the experimental $T_c(P)$ data obtained by Môri et al. [32], and compare with results of the following calculations. In order not to retain too many variable parameters, the analysis is based on $T_c = 117 \text{ K}$ at $P = 0$ [32], $\beta = 0.15 \text{ au}^{-2}$ and $\beta = 0.175 \text{ au}^{-2}$,

$\langle A\omega \rangle = 200$ K, $T_{c,m} = 122$ K. Variations of the latter two parameters to 220 K for $\langle A\omega \rangle$, 127 K for $T_{c,m}$, are found to yield only minor changes in $T_c(P)$. The bulk modulus B is not known for $N = 2$; a model calculation by Cornelius and Schilling [45] results in $B = 103, 105$, and 106 GPa for $N = 1, 2$, and 3 , respectively. Experimentally, $B = 82$ GPa for $N = 1$ [46]; comparing with the model results [45] we adopt a trial value $B = 85$ GPa for both $N = 2$ and $N = 3$.

The effect of pressure on T_c was evaluated for both overdoped ($\kappa > \kappa_m$ at $P = 0$) and underdoped ($\kappa < \kappa_m$ at $P = 0$) systems, with pressures up to 30 GPa, following the usual procedure. With $\beta = 0.15 \text{ au}^{-2}$, dT_c/dP at $P = 0$ is found to be $+1.6$ K/GPa for over-(abbreviated “ov”), $+1.5$ K/GPa for underdoped (“un”) systems, with maximum T_c of 133 K (ov), 145 K (un), at pressures $P = 17$ –18 GPa (ov) and 29 GPa (un). On the other hand, with $\beta = 0.175 \text{ au}^{-2}$ we obtain $dT_c/dP = 0$ K/GPa (ov), $+0.7$ K/GPa (un); T_c for the overdoped system continuously decreases, reaching a value of 25.5 K at $P = 30$ GPa. In the underdoped case, a maximum T_c of only 121 K is reached, at $P = 10$ GPa. The results for an *underdoped* system strongly resemble those for $\text{Hg}(N = 2)$ at $\beta = 0.15 \text{ au}^{-2}$ and $\beta = 0.175 \text{ au}^{-2}$, as expected.

We conclude that *none* of the calculated results even qualitatively reproduces the experimental [32] $T_c(P)$ behavior of a maximum $T_c \approx 119$ K at a pressure of 1.9 GPa, with an initial slope $dT_c/dP = +1.7$ K/GPa. Extrapolating from the observed essential differences between results obtained with low- T and high- T application of pressure, the cause of this disagreement is assumed to arise from the fact that in the experiment pressure was applied *at room temperature*. We emphasize that an accurate analysis of these phenomena clearly lies outside the scope of the present approach. Nevertheless, we can proceed semi-empirically on the basis of expression (12) for the change of β with P , by substituting on the right-hand side of (12) the experimental value $d \ln T_c/dP = 1.7/117 \text{ GPa}^{-1}$, while selecting $\beta = 0.175 \text{ au}^{-2}$, and an underdoped system as the only possible starting point for approaching the experimental behavior of $T_c(P)$. This procedure is similar to the one adopted for $\text{Ti}_2(N = 1)$ discussed earlier.

The calculation applying (12) leads to a value $d\beta/dP = 5.25 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$, indeed larger than the “low-temperature” result $d\beta/dP = 2\beta/3B = 1.37 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$. The conclusion is that at room temperature some oxygen diffuses from the $(\text{Ti-O})_2$ bilayers towards the CuO_2 layers in this system. We note the difference with overdoped $\text{Ti}_2(N = 1)$, in which case $d\beta/dP$ was always *smaller* than $2\beta/3B$. We now use $\beta(P) = \beta_0 + (d\beta/dP)P$, instead of $\beta_0 \exp(2P/3B)$, and determine $T_c(P)$, comparing with the values up to $P = 8$ GPa obtained by Mōri et al. [32]. The results are striking indeed: T_c increases from 117 K at $P = 0$ to a maximum of 118.8 K at $P = 2$ GPa, compared with ≈ 119 K at $P = 1.9$ GPa experimentally; at $P = 4$ GPa, $T_c = 117.1$ K. For higher pressures, the calculated T_c decrease more steeply than the experimental values, possibly indicating that the assumed linear relationship between $[\beta(P) - \beta_0]$ and P holds only for not too large P .

In Fig. 6a we show the results of the calculation for underdoped $\text{Ti}_2(N = 2)$ with $\beta = 0.15 \text{ au}^{-2}$ and 0.175 au^{-2} assuming low-temperature application of pressure,

Fig. 6. (a) Calculated $T_c(P)$ values for underdoped $Tl_2(N=2)$ with '2D' ($\beta = 0.15 \text{ au}^{-2}$, upper curve) and '3D' ($\beta = 0.175 \text{ au}^{-2}$, lower curve) behavior, and pressure up to 30 GPa assumed to be applied at low temperatures. (b) Calculated $T_c(P)$ values for underdoped $Tl_2(N=2)$ as a '3D' system ($\beta = 0.175 \text{ au}^{-2}$), for pressure up to 8 GPa applied at room temperature, taking pressure-induced diffusion of oxygen anions from the $(Tl-O)_2$ bilayers into account (see text). A maximum T_c of 118.8 K (exp. 119 K) at $P = 2$ GPa (exp. 1.9 GPa) is found. Exp. values from [32].

i.e. with $d\beta/dP = +1.37 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$ up to $P = 30$ GPa, and in Fig. 6b those for $d\beta/dP = 5.25 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$ in the pressure range 0–8 GPa. The curves of Fig. 6a are predicted results for low- T pressure application ($\beta = 0.15 \text{ au}^{-2}$ for "2D", $\beta = 0.175 \text{ au}^{-2}$ for "3D" behavior). The close agreement with experiment for $d\beta/dP = 5.25 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$ and $\beta = 0.175 \text{ au}^{-2}$ (Fig. 6b) implies that the system

investigated by Mōri et al. [32] has 3D characteristics, *in contrast* with $\text{Hg}(N = 2)$ studied experimentally by Gao et al. [12,31] and by Kosuge et al. [38] with a maximum T_c of 154 K at $P = 29$ GPa. We finally note that selecting $\beta = 0.15 \text{ au}^{-2}$ for $\text{Tl}_2(N = 2)$ leads to a value $d\beta/dP = 1.32 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$, very close to the “low- T ” value $2\beta/3B = 0.30/255 = 1.18 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$. The resulting $T_c(P)$ curve is practically identical with the one for $\beta = 0.15 \text{ au}^{-2}$ in Fig. 6a, i.e. no maximum is found in the low- P range.

5.2.4. $\text{Tl}_2(N = 3)$

To conclude the analysis of superconductivity in the $\text{Hg}(N)$ and $\text{Tl}_2(N)$ series we discuss $\text{Tl}_2(N = 3)$, i.e. $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$, with $\delta = 0$ for nominal composition. The most detailed experimental results of this system were given by Jover et al. [11]: with an initial $T_c(P = 0)$ of 128.5 K (zero resistivity at 125.1 K) and a slope $dT_c/dP = 1.75 \text{ K/GPa}$, a maximum T_c of 133 K is reached at $P = 4.2$ GPa. Pressure was applied at room temperature. For the calculations we proceed in a similar way as with $N = 2$, choosing for the parameters $T_{c,m}$, $\langle A\omega \rangle$ the values 133.5 K and 200 K, respectively. Minor changes to 129.5 K and 138.5 K for $T_{c,m}$, 220 K for $\langle A\omega \rangle$, are found to entail insignificant changes in $T_c(P)$. For the bulk modulus we adopt the value $B = 85 \text{ GPa}$, as mentioned above.

The dependence of T_c on pressure was evaluated for both overdoped ($\kappa > \kappa_m$ at $P = 0$) and underdoped ($\kappa < \kappa_m$ at $P = 0$) systems (marked “ov” and “un”, respectively) for pressures up to 30 GPa, as before, taking limiting β values of 0.15 au^{-2} (decoupled CuO_2 layers) and 0.185 au^{-2} (nominal composition, see Section 3). We first summarize the results for $T_c(P)$ when pressure is applied at low temperatures, following the usual procedure by considering only the effect of volume changes on the parameters κ and β given by (10). With $\beta = 0.15 \text{ au}^{-2}$ we obtain an initial slope $dT_c/dP = +1.3 \text{ K/GPa}$ (ov) and $+1.4 \text{ K/GPa}$ (un), a maximum $T_c(\text{ov})$ of 140 K at $P = 15$ GPa, and a $T_c(\text{un})$ of 154 K at 28 GPa. As with $\text{Tl}_2(N = 2)$, the underdoped system behaves much the same as $\text{Hg}(N = 3)$, with a maximum critical temperature in excess of 150 K and a corresponding pressure close to 30 GPa. For the other limit $\beta = 0.185 \text{ au}^{-2}$, and an overdoped system, $dT_c/dP = -0.8 \text{ K/GPa}$, decreasing continuously to 11 K at $P = 30$ GPa. The underdoped $\text{Tl}_2(N = 3)$ has a calculated dT_c/dP of $+0.3 \text{ K/GPa}$, and T_c reaches only 129.4 K at $P = 4\text{--}5$ GPa. A plot of these results is given in Fig. 7a.

Comparing with the experimental maximum T_c of 133 K at $P = 4.2$ GPa, the conclusion is that all calculated results deviate even *qualitatively* from the observed behavior, for which the effect of diffusing oxygens at room temperature from the bilayers is assumed to be responsible. Again, we now proceed semi-empirically by substituting the observed $d \ln T_c/dP = 1.75/128.5 \text{ GPa}^{-1}$ into the right-hand side of (12), leading to a value $d\beta/dP$ for every β . Adopting these values in $\beta(P) = \beta_0 + (d\beta/dP)P$, instead of (“low- T ”) $\beta(P) = \beta_0 \exp(2P/3B)$, yields $T_c(P)$ as a function of β .

Surprisingly, the only possible solutions are found for β close to 0.17 au^{-2} (underdoped systems); with $\beta < 0.165 \text{ au}^{-2}$, $T_c(P)$ increases continuously with pressure in

Fig. 7. (a) Calculated $T_c(P)$ values for underdoped $Tl_2(N=3)$ with '2D' ($\beta = 0.15 \text{ au}^{-2}$, upper curve) and '3D' ($\beta = 0.185 \text{ au}^{-2}$, lower curve) behavior, and pressure up to 30 GPa assumed to be applied at low temperatures. (b) Same as in Fig. 6b, this time for $Tl_2(N=3)$, with a β value 0.17 au^{-2} , taking into account the effect of pressure-induced diffusion of oxygen anions from the $(Ti-O)_2$ bilayers (see text). A maximum T_c of 132.5 K is found (exp. 133 K), at a pressure of 4–5 GPa (exp. 4.2 GPa). Exp. values from [11]; pressure applied at room temperature.

the range 0–8 GPa, whereas for $\beta > 0.175 \text{ au}^{-2}$, $T_c(P)$ decreases with P . These results are illustrated in the following Table 4.

The values of $d\beta/dP$ are consistently larger than the "low- T " $2\beta/3B$ (between 1.25 and $1.37 \times 10^{-3} \text{ au}^{-2}/\text{GPa}$), implying that oxygen anions diffuse under pressure. The value $\beta = 0.17 \text{ au}^{-2}$, with maximum T_c of 132.7 K at a pressure of

Table 4

Calculated values $T_c(P)$ for underdoped $Tl_2(N = 3)$ in the pressure range 0–8 GPa, with pressure applied at ambient temperature. The change $d\beta/dP$ was evaluated using the observed $d \ln T_c/dP$ [11] (see text). A maximum T_c of 132.7 K (exp. 133 K) is found at a pressure of 4.3 GPa (exp. 4.2 GPa). Exp. values from [11].

$\beta(\text{au}^{-2})$:	0.160	0.165	0.170	0.175	0.180
$d\beta/dP(10^{-3}\text{au}^{-2}/\text{GPa})$:	2.25	2.87	3.91	6.11	14.09
$P(\text{GPa})$: 0	128.5	128.5	128.5	128.5	128.5
1	130.2	130.1	130.1	129.8	127.6
2	131.7	131.6	131.3	130.2	119.5
3	133.2	132.9	132.1	129.4	94.1
4	134.5	133.9	132.5	127.4	10.2
5	135.7	134.8	132.5	123.5	0
6	136.8	135.5	132	117	0
7	137.8	135.9	130.9	106.3	0
8	138.6	136.1	129.1	88.4	0

4.3 GPa leads to *excellent* agreement with experiment (133 K at 4.2 GPa). A plot of $T_c(P)$ for $\beta = 0.17 \text{ au}^{-2}$ in the range $P = 0$ –8 GPa is presented in Fig. 7b.

To find a possible explanation for the calculated, unexpected, β value of 0.17 au^{-2} we surmise that it is due to specific composition of the sample on which the experiments [11] were carried through. The reported starting composition [47] was $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10+\delta}$, substantially off-stoichiometric, on which several processes were carried out (vacuum annealing accompanied by Tl losses, final annealing in 0.2% oxygen). It is impossible to assess the remaining concentration of oxygen (O^{2-}) anions after such treatment (a loss of 10% O^{2-} leads to a decrease in β from 0.185 to 0.172 au^{-2}).

6. Summary of results and concluding remarks

We have presented a quantitative analysis of superconductivity in the $Hg(N)$ and $Tl_2(N)$ cuprates with $N = 1, 2$, and 3 CuO_2 layers per molecular unit, and with chemical composition $HgBa_2Ca_{N-1}Cu_NO_{2N+2+\delta}$ and $Tl_2Ba_2Ca_{N-1}Cu_NO_{2N+4+\delta}$, respectively. As in earlier work, Cooper pair formation was supposed to be effected through indirect exchange pairing between conduction electrons via closed-shell oxygen (O^{2-}) anions; it is a consequence of the Pauli principle for overlapping conduction and (oxygen) valence wavefunctions. The coupling strength $|W|$ in equation (1) for the critical temperature is a function of three parameters α , β , and κ , with α a Gaussian parameter in the Wannier function for the oxygen valence band, β a Gaussian parameter in the theta function for the conduction electrons, and $\kappa = bk_F/\alpha^{1/2}$, with k_F the length of the Fermi vector and b a materials constant for the cuprates. We use an effective-mass approximation with $m^*/m_e = 5$; m_e is the mass of a free electron. We calculated the critical temperature T_c as a function of external

pressure, introducing also a critical temperature $T_{c,m}$ as the maximum temperature attainable while varying only κ (thus k_F) at zero pressure, keeping β constant; the associated κ is denoted as κ_m . A system with $\kappa < \kappa_m$ is called *underdoped*, for $\kappa > \kappa_m$ it is called *overdoped*. For the calculation of $T_c(P)$ we must in general consider both possibilities in a comparison with experiment.

The results may be summarized as follows:

(i) $Hg(N = 1)$ and $Tl_2(N = 1)$ (Section 5.1)

The results for $Hg(N = 1)$ are given in Table 1 and plotted in Fig. 2 (P up to 30 GPa), and are found to be in quantitative agreement with experiment for an underdoped system at ambient pressure. The results for $Tl_2(N = 1)$ were compared with experimental values of $T_c(P)$ obtained by Sieburger and Schilling [33] in the range $P = 0$ –0.6 GPa for different T_c at $P = 0$ (different excess oxygen content). In these experiments pressure was applied (or changed) at 10 degrees above the measured T_c . The calculated $T_c(P)$ are collected in Fig. 3, and a comparison with experiment [33,36] is given in Table 2, showing detailed agreement. The anomalous behavior of T_c with pressure applied at *room temperature* was found to be caused by pressure-induced diffusion of oxygen anions from the $(Tl-O)_2$ bilayers towards the CuO_2 layer. Results of that calculation are presented in Table 3.

(ii) $Hg(N = 2, 3)$ and $Tl_2(N = 2, 3)$ (Section 5.2)

The high maximum T_c of 154 K measured by Gao et al. [12,31] in $Hg(N = 2)$ at a pressure of 29 GPa is quantitatively reproduced on the basis of the assumption that superconductivity in this compound is a *two-dimensional* (2D) phenomenon (decoupled CuO_2 layers) except for optimal oxygen loading where Chen et al. [24] observed a *break* in the $T_c(P)$ curve at $P = 0.4$ GPa, with a slope dT_c/dP reduced by a factor of about 2. We interpreted this discontinuity in the slope as a transition to 3D superconductivity. Comparing results for (3D) $\beta = 0.175 \text{ au}^{-2}$ and (2D) $\beta = 0.150 \text{ au}^{-2}$, it was found that the observed reduction in dT_c/dP is indeed obtained.

The system $Hg(N = 3)$ shows a similar 2D behavior, reaching a calculated maximum critical temperature close to 160 K at a pressure of 30–31 GPa, in substantial agreement with the experimental values of Gao et al. Both the $N = 2$ and $N = 3$ systems are found to be underdoped with respect to κ_m .

No $T_c(P)$ values are available for $Tl_2(N = 2)$ or $Tl_2(N = 3)$ from experiments in which pressure is applied (or changed) at low temperatures. The calculated $T_c(P)$ curves (Figs. 6a and 7a) are very similar to those of $Hg(N = 2)$ and $Hg(N = 3)$, respectively, for both 2D and 3D systems. To compare with experiments in which pressure was applied at ambient temperature ([32] for $N = 2$, [11] for $N = 3$) we proceeded semi-empirically as with the $N = 1$ compound. Excellent agreement with experiment was established ([32]: maximum $T_c \approx 119$ K at $P = 1.9$ GPa) for $N = 2$ and a *three-dimensional* interpretation of superconductivity (Fig. 6b), in contrast with $Hg(N = 2)$. For $Tl_2(N = 3)$, the observed maximum T_c of 133 K at $P = 4.2$ GPa [11]

was found for a β value of 0.17 au^{-2} (Fig. 7b) instead of (3D) $\beta = 0.185 \text{ au}^{-2}$ or (2D) $\beta = 0.15 \text{ au}^{-2}$. This deviating behavior was ascribed to specific (off-stoichiometric) composition of the sample used in the experiment.

As a final item, we comment briefly on the results of three recent doping experiments with high- T_c cuprates. First, Niedermayer et al. [48] measured muon-spin depolarization rates in oxygen-excess $\text{Ti}_2(N = 1)$ with T_c values of 84, 66, 53 and 13 K. The depolarization rate σ_0 (i.e. $\sigma(T)$ extrapolated to $T = 0$) was found to decrease proportional to the decreasing T_c . In the London model $\sigma_0 \propto \lambda^{-2} \propto n_s/m^*$, with λ the London penetration depth, n_s the superfluid density, and m^* the effective mass of the carriers. Within this framework, the authors conclude that apparently the superfluid density decreases with decreasing T_c . This phenomenon is in contrast with studies on high- T_c cuprates in the oxygen-deficient region, where σ_0 increases with k_F . It was proposed that a pair-breaking mechanism operates in the oxygen-excess region, decreasing both T_c and n_s .

This phenomenon is readily explained on the basis of indirect-exchange pairing without invoking a pair-breaking mechanism. Assuming, as the authors do, that overdoped oxygen is incorporated in the $(\text{Ti}-\text{O})_2$ bilayers as hole dopants, the situation is much like that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system in the Sr-overdoped region, for which T_c steeply decreases with increasing x . As a result, in spite of an increasing carrier density, the coupling strength $|W|$ rapidly falls, leading to a decrease in muon-spin depolarization rate σ_0 , as observed.

A second recent paper, by Song et al. [49], deals with ^{63}Cu NMR Knight shift and magnetic susceptibility measurements on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for $x = 0, 0.10, 0.16$ and 0.20 in the normal and superconducting states. The results show that, with increasing Sr doping, the spin susceptibility of the carriers increases monotonically from $x = 0.10$ to 0.20 , i.e. *without* showing sign of a van Hove singularity near maximum T_c (for $x \approx 0.15$). Second, there is a “smooth evolution in the spin susceptibility from a regime of strong singlet correlations among carriers, to one where they are relatively weak”. This finding reflects the evolution of the indirect-exchange coupling strength $|W|$ with increasing k_F in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [28].

Lastly, we mention a paper by Kataev et al. [50] concerning measurements of the EPR linewidth of $(0.01) \text{ Gd}^{3+}$ nuclear spins doped into $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, with $x = 0.08\text{--}0.35$. These measurements make it possible to evaluate the evolution of the density-of-states with doping level x via the measured temperature dependence of the dopant-spin relaxation rate. The authors interpret their results on the basis of the BCS electron-phonon expression $T_c = \langle\omega\rangle \exp(-1/\lambda)$; $\lambda = N(E_F)V_{\text{el-ph}}$, for x -independent average phonon frequency $\langle\omega\rangle$. Their conclusion is that up to the optimum value $x = 0.15$ the coupling strength λ increases with x , whereas for larger x it decreases. It is supposed that either in the overdoped region the coupling strength λ ceases to be a linear function of the density-of-states or there occurs an additional decoupling (repulsive) interaction which decreases λ . On the basis of indirect-exchange pairing the explanation of these phenomena lies in the effect of $\kappa = bk_F/\alpha^{1/2}$, which at higher doping causes a rapid decrease of the coupling $|W|$.

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