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Reinterpretation of femtosecond laser pump–probe and thermomodulation optical spectroscopy results on HTSC materials in terms of the resonant negative-U model

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Abstract. The laser pump/probe spectroscopy from Stevens *et al* (on $YBCO_7$) and the thermomodulation optical data and analysis from Holcomb *et al* (on a selection of HTSC materials) are examined in terms of the resonant negative-U mechanism for high temperature superconductivity (HTSC) in the mixed-valent cuprates. The work centres on the universal 1.5–2 eV features becoming visible below T_c upon the optical 'charge-transfer' edge. These it is argued are not simple p-to-d band-to-band excitations but are to be associated with the mixed-valent and negative-U states that instigate HTSC. This argument is supported both by the decay characteristics apparent in the new data recorded by Stevens *et al* and also in the outcome of the Eliashberg analysis developed by Holcomb *et al* to accommodate their own thermomodulation data. The interpretation provided is in line with that offered recently of the highly characteristic thermoelectric behaviour exhibited by all HTSC systems.

In order to demonstrate the applicability of any proposed HTSC mechanism a very direct route is to turn to the detailed structure of the additional excitation channels introduced into the system. This entails probing directly those states and conditions which instigate and support the superconductivity. In this, optical work offers a sensitive, widely applicable and highly discriminatory tool. That is particularly so with the advent of femtosecond laser 'pump–probe' spectroscopy, wherein the time scale and excitation energy are adjustable to the relevant electronic processes. In the present paper we wish to recast and extend the discussion given by Stevens *et al* [1] of their very revealing pump–probe experiments on $YBa_2Cu_3O_7$ ($YBCO_7$) crystals and films. This will be done in terms of the resonant negative-U model for HTSC developed in my earlier papers [2]. Stevens *et al* themselves turned to the standard LDA band structure in seeking to identify the electronic transitions to which their 1.5 eV probe radiation was resonantly coupled, in particular once below T_c. In contrast the interpretation to be developed below ascribes the activity to more localized states, in a scenario more appropriate to the actual circumstances of the mixed-valent HTSC cuprates. This provides opportunities for much more of the detail within the spectra to be comprehended. The treatment embraces in particular the generality of the observed effects, further witnessed to by the complementary thermomodulation optical spectroscopy data secured by Holcomb *et al* [3] from four quite different HTSC cuprate systems.

The laser pump–probe experiment employs a 1.5 eV Ti:sapphire laser, which was frequency doubled to supply a 3 eV photon pump to the sample. The power is delivered in the form of 150 fs pulses (broadened to 2 ps by the modulator) at a repetition frequency of 80 MHz. The laser fundamental itself was used as subsequent 1.5 eV probe of the conditions generated by the 3 eV pumping. In several more standard optical measurements on the HTSC

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'metals' (see figure 1 of [1]) it has been observed that once below T_c a characteristic absorption feature becomes apparent sitting upon the leading 'charge transfer' edge. The feature is quite distinct from the excitons of the parent (d^9) Mott-insulating phase (1.5 eV, versus 1.8 eV for the latter in the $YBCO_{7-\delta}$ family). As was stated above, Stevens *et al* attempted to relate this new absorption feature to standard p-to-d interband transitions which in some way are coupled into the superconductive process. However in what follows the extra absorption at 1.5 eV will be attributed to *two* novel types of electronic excitation—(1) from the Fermi level, and (2) from a many-body metastable fluctuational state virtually degenerate with E_F. This in both cases is to attain the 'dopant' excited state condition designated in my earlier work by $^9Cu^{1-}_{III}$ [2]. (For a recap on the meaning of symbols like the latter see the figure caption of the present paper.)

A portrayal of the advocated negative-U scheme was made in figure 1 of Wilson and Zahrir [2] or again in the figure on p 346 of Wilson (1994) [2], and this has been incorporated now into the present figure 1 with much better defined numerical precision. The modelling introduced in [2] registers the negative-U local-pair transient state—identified as $^{10}Cu^{2-}_{III}$—as being virtually degenerate (at optimal doping) with the free-carrier Fermi level. Note E_F of course has to be common to the entire, inhomogeneous, two-subsystem mixed-valent material (figure 1, Wilson 1997 [2]). The above doubly loaded fluctuational state constitutes a negative-U one in that successive Cu_{III} site electronic loadings $^8Cu^0_{III} \rightarrow {}^9Cu^{1-}_{III} \rightarrow {}^{10}Cu^{2-}_{III}$ form a 're-entrant' sequence, energy-wise. This reversal is understood as issuing from the very strong correlation effects associated with the local $(p^6)d^{10}$ shell closure attained and the concomitant collapse of the large p/d antibonding elevation experienced by the $e_g pd\sigma^*$ states ($d_{x^2-y^2}$ and d_{z^2}). This is the result in particular of the shell closure being incurred within a raised-valent local environment [2].

Above T_c there is perceived from specific heat work, etc to be rather a small local-pair population established [2]. The number and coherence of local pairs instigating the superconductivity increases very sharply upon passage below T_c—a consequence of the resonant energy location of the negative-U state, as expounded on below. In a homogeneous structure (as distinct from the current mixed-valent one) any such state inversion would simply be referable to as a $U_{eff} < 0$ circumstance in standard Hubbard terminology. However the present two-sub-system situation is more intricate. In the HTSC materials, in order to attain the present negative U, the strong shell-closure correlations at p^6d^{10} incurred with the double-loading fluctuation $^{10}Cu^{2-}_{III}$ have to more than counter the inevitable very sizeable Coulomb repulsion term, $+U_C$. The latter is widely accepted as $\sim$4 eV. With the inhomogeneous mixed-valent HTSC cuprates, distinction must be registered between the two states $^{10}Cu^{2-}_{III}$ and $^{10}Cu^{1-}_{II}$, each a fluctuational completion of the key topmost, $x^2 - y^2$ symmetry, $dp\sigma^*$-antibonding band. Throughout [2] the HTSC phenomenon has been presented as being driven by the former of these states, $^{10}Cu^{2-}_{III}$, the 'double-loading' fluctuation secured under high-valent local coordination. The significant difference in energy between the above two d^{10} fluctuational conditions arises from the marked differences in their associated local Madelung potentials, radial extension of the wavefunctions involved and local bond length adjustments.

What the pump–probe experiments of Stevens *et al* [2] on $YBCO_7$ have revealed is that *two* kinds of introduced *secondary* excitation are (i) executed under, and (ii) tracked as a function of time by the subsequent 1.5 eV *probe* radiation. Those electrons recording the '*differential*' (change when pumped/unpumped) modification in the probe's action/signals are the ones which arrive transiently in the vicinity of E_F, following upon the *primary* pumping high intensity radiation pulse. They come from states up to 3 eV deeper within the valence band. As stated, two optical components are upon close inspection observed to be present within

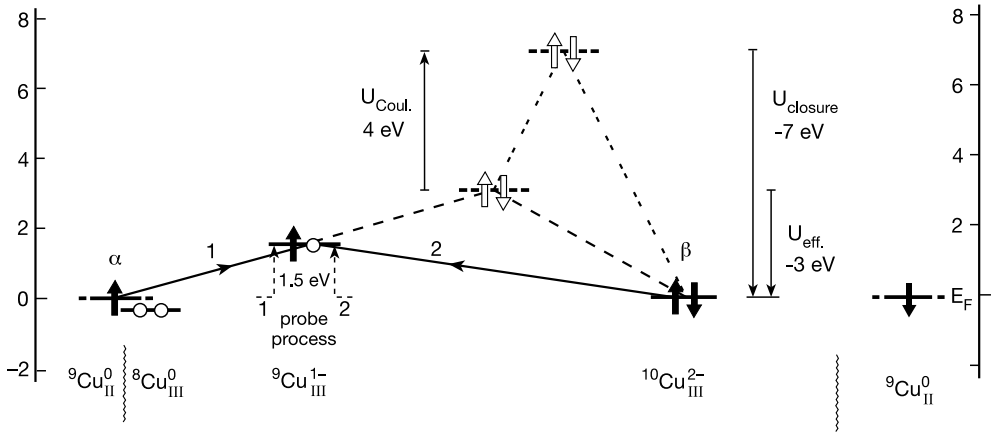

Figure 1. Resonant negative-U modelling from [2], where the state symbols used are introduced. The latter indicate a local coordination unit's nominal cation valence along with its instantaneous charge loading, both current and as a deviation from the norm. The figure indicates the fluctuation state-loading energies across the trivalent ('dopant') site-loading sequence $^8Cu^0_{III}$, $^9Cu^{1-}_{III}$, $^{10}Cu^{2-}_{III}$ to be a re-entrant one. This is due to shell closure and the accompanying collapse in $p/d\,\sigma/\sigma^*$ interactions. Because of some permanent, metallizing, charge transfer between the two sub-systems in the mixed-valent situation, ground states $^9Cu^0_{II}$ and $^8Cu^0_{III}$ are effectively brought to a common Fermi energy. In optimally doped HTSC systems the negative-U double-loading fluctuation state $^{10}Cu^{2-}_{III}$ is set resonant with E_F; this makes U_{eff} (per electron) $= -1.5$ eV, in line with the value supported by the present experiments.

Probe excitation process 1 involves a laser resonant 1.5 eV elevation of (hot) 'quasi-particles' from E_F in an inter-sub-system charge transfer excitation to give $^9Cu^{1-}_{III}$: this transfer is pre-empted to some degree through the 3 eV primary pumping. The probe reveals for the above hot quasi-particle population (α) a relatively fast decay (3 ps)—though slow for a normal metal. Probe excitation process 2 monitors by contrast the transient population of pump-produced species β, namely the metastable local pairs $^{10}Cu^{2-}_{III}$ for which the decay time is much longer ($\sim$10 ns).

Note customary definition $U = [(E_{n+2} - E_{n+1}) - (E_{n+1} - E_n)] = (E_{n+2} + E_n) - 2E_{n+1}$ becomes in the present case $U = E(d^{10}) + E(d^8) - 2E(d^9)$, where $U = U_{effective} = U_{Coul} - U_{shell\ closure}$. With $U_{Coul} = +4$ eV and $U_{shell\ closure} = -7$ eV, we reach $U_{eff} = -3$ eV per pair or 1.5 eV per electron, as the present experiments would endorse.

the given probe's fixed energy signal (1.5 eV here). These we take to relate to two distinct products of significant lifetime ($\geqslant 10^{-12}$ s) generated as a result of the primary excitation. The two primary-excited species are actually revealed through the corresponding probe excitation signals to possess very distinct decay rate characteristics. Of the two *pump*-generated species, one (α) is monitored by the probe in secondary process 1 to have a rather moderate half-life $\sim$3 ps. By contrast the second species β, monitored in process 2, has not decayed away totally prior to the next pulse of primary radiation being received ($\tau \sim 10$ ns) (see [1], figure 2). This long-lived (metastable) β species would appear to be created under the primary pumping in numbers $\sim$2 to 10 times less than for the shorter-lived α state, details dependent upon the temperature ($T < T_c$).

The two monitoring secondary probe excitations register appropriate modification in all the various aspects of the normalized *incremental* optical response. Those aspects are tracked then (at 1.5 eV) as functions of time and of temperature. For single crystals it actually is easiest to measure the relative reflectance change $\Delta\mathcal{R}/\mathcal{R}$, while for thin film samples it is the transmittance change $\Delta\mathcal{T}/\mathcal{T}$ which is the quantity recorded. Note, since $\mathcal{T} = 1-(\mathcal{R}+\mathcal{A})$, that $\Delta\mathcal{T} = -(\Delta\mathcal{R}+\Delta\mathcal{A})$. This inter-relation between $\Delta\mathcal{T}$, $\Delta\mathcal{R}$ and $\Delta\mathcal{A}$ can be quite complicated, particularly when expressed through fractional changes as in the present work. Stevens *et al*

Table 1. Representative data at 50 K abstracted from the pump–probe optical results of Stevens *et al* [1] on YBa_2CuO_7 for 1.5 eV probe energy. The signal for process 1 decays over a time scale of picoseconds and that of process 2 over tens of nanoseconds.

	Fractional 'differential' probe signals ($\times 10^{-5}$)				
(50 K)	$\Delta\mathcal{R}/\mathcal{R}$	$\Delta\mathcal{A}/\mathcal{A}$	$\Delta\mathcal{T}/\mathcal{T}$	Biggest $\Delta\mathcal{T}/\mathcal{T}$	$\Delta\mathcal{T}(T_c)$
process 1 re α (hot e at E_F+)	+3.5	−1.5	−2	at 0 K	$0-\varepsilon$
process 2 re β ($^{10}Cu^{2-}_{III}$)	−0.25	+0.5	−0.25	75 K	0

observe that changes of sign and relative magnitude as a function of T occur quite differently between the above two species. Table 1 provides a brief overview of the actual data at a temperature intermediate between 0 K and T_c. In all circumstances note that $\Delta\mathcal{T}$ emerges as negative (see inset to figure 2 in [1]). The fractional differential change $(\Delta\mathcal{T}/\mathcal{T})_{1.5\text{ eV}}$ in fact is only $\sim 1\times 10^{-5}$ under the operating conditions, but this is readily measurable when using 2 MHz modulated spectroscopy.

Despite the two probe signals suffering very significant and characteristic changes in *intensity* following passage below T_c, the pumped state decay *rates* themselves appear more or less temperature independent. A further telling observation is that both optical signals become very small when the polarization directions for pump and probe are together selected to be $\|_c$ (see figure 3, [1]). Once again this reflects the dominantly basal-plane character to the cuprate HTSC phenomenon. Below we shall examine in detail the differences in sign, magnitude and temperature dependence of the various probe-resonant 1.5 eV signal intensity changes (in absorption, reflection and transmission). This will permit us to reach a justifiable identification of the two populations α and β established via the primary pulses. The marked distinction in lifetime of the two pumped species offers the key.

The faster-decaying pumped species α, monitored in probe process 1, is understood to be 'hot' single electrons settled out to near E_F. These then become further excited by the *probe* back up from E_F in an effectively intersub-system intersite 'charge transfer', i.e. a promotion to the condition $^9Cu^{1-}_{III}$. The several picosecond lifetime of the above pump-excited quasi-particle population α expresses the considerable local inhomogeneity inherent to HTSC 'metals'. Because of the mixed-valent disorder and the proximity to the Mott–Anderson transition, the ordinary ('cold') quasi-particles often experience weak localization in HTSC materials. This is directly evident from Seebeck (Wilson 1997) [2] and Hall results [4], and likewise from the resistivity data of Ando *et al* [5] obtained under ultra-high magnetic fields. By most measures it is well established that the HTSC materials are far from supporting a simple uniform Fermi liquid. The current, valence-band-disturbed, pumped centres will augment the partial localization, extending trapped quasi-particle lifetimes. The Fermi level within the mixed-valent HTSC superconductors is dominantly set by the majority configuration $^9Cu^0_{II}$. The added minority trivalent sites $^8Cu^0_{III}$ then are brought to a common chemical potential through permanent, slight, inter-sub-system charge transfer from Cu_{II} to Cu_{III}. The probe-induced excitations of process 1 above are in excess of such 'natural' transfer (as, of course, of any produced directly by the *pump*). Note that at 1.5 eV, the above-postulated inter-sub-system charge transfer excitation has become 'accidentally' resonant with the probe energy involved when employing the Ti:sapphire laser. For the effect of changing lasers see below.

Directly following upon the primary pumping a somewhat *reduced* effective population of *un*changed ('empty' $d^0_{x^2-y^2}$) Cu_{III} centres will automatically present itself to the *secondary* resonant absorption process—one identical to intersite, mixed-valent charge

transfer. As may be seen from the inset to figure 2 of the paper of Stevens *et al*, the resulting combination (at 1.5 eV) of a somewhat reduced (temporarily blocked) absorptivity plus an appreciably augmented reflectivity (resulting from detrapping) leads to a complementary reduction in the relative *incremental* (change when pumped/unpumped) transmissivity signal. This negative incremental $\Delta\mathcal{T}$ signal becomes considerably larger upon cooling below T_c. That is because additionally the pumping prevents the normal quasi-particle population becoming abstracted into the paired-state condensate. Indeed once below T_c the 'differential' probe signal $(\Delta\mathcal{T}/\mathcal{T})_{1.5\text{ eV}}$ associated with process 1 and population α is demonstrated by Stevens *et al* to track in magnitude the superconducting order parameter, $\Delta(T)$; this it does while adhering throughout to the appropriate negative sign ([1], figure 4].

The probe signal associated with the second channel of 1.5 eV probe excitation sets in significantly only upon cooling below T_c. The relatively very long lifetime associated with β, the second pumped species, would indicate that in this case we are involved with a highly metastable entity, once below T_c; a product now virtually freed from strong scattering by the quasi-particles. It constitutes a state of sufficient (pumped) population as to be able to support a differential probe signal not too dissimilar in intensity from that associated with species α. The candidate state which we are proposing for species β has at the outset been indicated to be the negative-U local-pair condition, $^{10}\mathrm{Cu}^{2-}_{III}$. The latter at optimal doping has earlier been deduced to be virtually degenerate with E_F (Wilson 1997) [2]. Accordingly the state is one capable of being monitored by the 1.5 eV probe. This is by virtue of 1.5 eV being the energy required to convert the double occupancy of the negative-U state back to single loading $^{9}\mathrm{Cu}^{1-}_{III}$, with the second electron relinquished to the Fermi sea (see figure 1). The probe signal magnitude is observed (at any given time lapse) to be linear with respect to the averaged power input from the pump. (The latter typically is just 60 mW distributed over a 200 μm diameter spot.) This observation would imply that species β is of sufficiently high population for it not to become exhausted under the secondary excitation—as could occur if defect based. From the inset to figure 2 in [1] it is evident that probe excitation process 2 monitoring species β is associated this time (i.e. under nanosecond delays) with a *positive* differential absorbance and a somewhat diminished (i.e. negative) differential reflectance (at 1.5 eV—see table 1). These changes combine to leave the size of the differential transmittance signal smaller, though remaining negative still as for process 1.

In the course of cool-down from T_c, the transmittance relating to species β and process 2 in fact displays a strikingly non-monotonic thermal evolution, quite different from species α in process 1 ([1], figure 5). Virtually identical changes have been recorded both for single-crystal and thin film samples. Immediately below T_c the pump-promoted double-occupancy local pair population brings a sharply diminished transmissivity towards the probe radiation. (Beware: the above specified figure presents the *modulus* of the differential transmissivity signal: compare inset to figure 2). However by 75 K (i.e. just 15 K below T_c in these samples), as the gap quickly opens up, the steep descent in differential transmissivity—or rather, the rise in absorptivity—terminates. There ensues then a steady return of the *differential* transmittance signal back towards zero, following a Boltzmann-like thermal decline. Probe signal 2 we see here as monitoring the pumped local-pair (β-species) population. These local pairs are progressively able to incorporate into the condensate, and become there less open to break up under the 1.5 eV probe radiation. Such compound excitation behaviour witnesses the large differential probe signal initially recorded when $T \sim T_c - \varepsilon$ steadily become diminished as pumped β species entities (along with any 'seeded' product pairs) are able thermally to incorporate into the coherent low temperature condensate. Indeed

it was found that the observed thermal 'deactivation' energy of the β population rapidly becomes recognizable below 0.7 T_c as the (approximately) zero-temperature superconducting gap, $2\Delta(0)$ ([1], figure 5). The interpretation given of the observed behaviour then is as follows. In the vicinity of T_c the pumped, metastable, negative-U, double-loading fluctuations, $^{10}\mathrm{Cu}^{2-}_{III}$, are agents for inducing HTSC in the overall system [2]. With the standard low temperature development of the superconducting state, more and more pumped electron pairs (β) become transferred into the superconducting condensate, this withdrawn fraction of the system growing on cooling as $\exp(2\Delta(T)/kT)$. The normalized incremental probe absorbance associated specifically (as signal 2) with optical disruption of the remaining *pumped* local pairs falls back steadily to yield the small residual $|\Delta\mathcal{T}/\mathcal{T}|$ signal observed. The curve fitting which Stevens *et al* actually employed below 70 K was a simplified Boltzmann one, based upon the zero-temperature (superconducting) gap parameter $2\Delta(0)$, rather than $2\Delta(T)$ itself. Nonetheless this proves sufficient to permit identification of the key activation process. Stevens *et al* observe that the energy which they extract roughly satisfies the weak coupling relation $2\Delta(0) = 3.5kT_c$. According therefore to the present scenario, both fast and slow decay signals recorded, each after their own fashion, hold direct association with states intimately involved in the proposed negative-U superconducting mechanism—primarily one of electronic origin.

At this point it is beneficial to recap the above discussion of the experimental results, making direct reference to our previously developed negative-U figure (figure 1 of Wilson and Zahrir [2] or figure on p 346 of Wilson 1994 [2]). We are able to repeat this now with closer precision as figure 1. As was stated above, both identified secondary excitations emerge with common energy—the 1.5 eV of the Ti:sapphire laser—as a result of the virtual degeneracy of the relevant initial states and the fact that the final state is identical ($^{9}\mathrm{Cu}^{1-}_{III}$). Explicitly we are ascribing to *probe* process 1 the essentially inter-sub-system charge-transfer excitation represented by

$$(\text{hot e at } E_F) \text{ into } {}^{8}\mathrm{Cu}^{0}_{III} \rightarrow {}^{9}\mathrm{Cu}^{1-}_{III} \qquad E_1 = 1.5 \text{ eV}$$

the hot electrons being the *pump*-produced species α. By contrast probe excitation 2 is asserted to commence not with the individual quasi-particles near E_F but instead is taken to involve optical disruption of the pump-generated, uncondensed pair states, $^{10}\mathrm{Cu}^{2-}_{III}$. The latter ($\beta$) are effectively virtually degenerate (per electron) with E_F in our favoured, resonant, negative-U modelling of figure 1, advocated earlier upon other grounds (Wilson 1997) [2]. This pair disruption is representable as

$$^{10}\mathrm{Cu}^{2-}_{III} \rightarrow (\text{hot e at} E_F) \text{ and } {}^{9}\mathrm{Cu}^{1-}_{III} \qquad E_2 = 1.5 \text{ eV}.$$

In the latter process the excitation energy is the energy per electron by which the double-occupancy fluctuational state $^{10}\mathrm{Cu}^{2-}_{III}$ is more stable than $^{9}\mathrm{Cu}^{1-}_{III}$ (the single-occupancy fluctuation into $^{8}\mathrm{Cu}^{0}_{III}$). This very sizeable state energy inversion, consequent upon strong reconstruction of local bonding interactions at the completion of the p and d shells, is what is understood as responsible for the marked metastability of the double-loading condition. A local lattice modification is the inevitable accompaniment to the full $\mathrm{p}^6\mathrm{d}^{10}$ electron shell closure experienced. The systematics of how the above vital 'negative-U' state inversion comes about in trivalent site-loading energies specifically for Cu_{III} have been set out in figure 3 of Wilson (1989) [2] and figure 3 of Wilson (1988) [2], where the above 1.5 eV energy difference was already surmised from the data then available.

The above pump–probe experiment was successively repeated employing alternative laser probe energies of 1, 2 and 3 eV. Very significantly the resulting dispersion behaviour found for the responses discussed above (inset to figure 4 of [1]) is in line with that from simple, directly measured, optical dispersion across the unusual band-edge feature around 1.5 eV detected

below T_c (see figure 1 of [1]). That likewise is the case for the more detailed examination of this same feature provided now by thermomodulation reflection spectroscopy [3]. In the latter work Holcomb *et al* reveal how this key absorption feature is quite universal to HTSC materials. Their experiments were performed using a ΔT modulation of 5 K with the radiation chopped at 20 Hz. The detailed analyses which they give of their results are expressed in the form of R_s/R_n plots. For the results to be significant when assessing the important changes that occur upon passage below T_c, the reflectivity changes have to be monitored at the level of 1 part in 10^5. A way needed to be found also to extrapolate the normal state signal through into the superconducting regime. This then permits evaluation of the screened plasma resonance frequencies (typically $h/\tau \sim 0.9$ to 1.5 eV). It emerged in this work, as observed from other areas (Wilson and Zahrir) [2], that $YBCO_7$ is unfortunately somewhat atypical in consequence of its 'Cu chains and planes' problem.

With the numerical information they had to hand, Holcomb *et al* [3] then proceeded to a full-scale iterative solution of the Eliashberg strong coupling treatment of the superconductivity, exploring various electron–boson spectral coupling functions, $G(\omega)$. After incorporating a typical value for the Coulomb repulsion factor $\mu^* \sim 0.15$, together with a $\tau_s(\omega)$ derived from the observed behaviour for $\tau_n(\omega)$, the inserted form of $G(\omega)$ was adjusted to match the experimental value of T_c. The optical observations would imply that $G(\omega)$ is probably going to consist of peaks in the phonon range and also around 1.5 eV. The heavy and necessarily high accuracy analysis proceeds through evaluation of the usual functions $Z(\omega, T)$ and $K(\omega, T)$ to reach $\Delta(\omega, T)$, the complex superconducting gap function. The process was carried out iteratively to a self-consistent outcome both in $\Delta(\omega, T)$ and $\tau(\omega, T)$, holding throughout to the requisite level of accuracy. The configuration of $G(\omega)$ needing to be inserted was examined additionally by use of the analytic Allen and Dynes equation in order to keep a check upon T_c. Following this very considerable effort, it was necessary finally, for comparison to be made to the experimental thermomodulation spectra, to compute the reflectivity ratio R_s/R_n versus energy. All this requires to be done for each of the materials and the temperatures examined. The outcome is that these authors were able to attain remarkably close fits to what was observed, particularly impressive in view of the somewhat uncertain form employed for $\tau_n(\omega, T)$. It would seem that the overall nature to the solution is both general and robust. To gain good fitting to the experimental spectra is found uniformly to demand the incorporation of a rather narrow peak into the coupling function $G(\omega)$ somewhere between 1.5 and 2.0 eV. The extracted superconductive coupling constant, λ, associated with this feature emerges in the elevated range of 1.35 to 1.5. The latter magnitude serves directly to emphasize the primarily electronic/excitonic and not phononic/structural mediation appertaining to HTSC.

Key, accordingly, to the HTSC problem is identification of the nature of the 1.5 eV feature active within $G(\omega)$. With the first part of this paper we have argued that this is not of simple band-to-band p-to-d charge transfer origin. Rather it marks the energy that governs the metastability of the negative-U state $^{10}Cu^{2-}_{III}$—expressly its binding energy (per electron) below single-occupancy $^{9}Cu^{1-}_{III}$. It is precisely this energy difference of 1.5 eV which locates the HTSC instigating local pair state at E_F, within the re-entrant state-loading sequence $^{8}Cu^{0}_{III}$–$^{9}Cu^{1-}_{III}$–$^{10}Cu^{2-}_{III}$. In the resonant negative-U modelling of the cuprates one thus arrives, under optimal doping conditions, at $U_{eff} = -1.5$ eV (per electron) as presented in figure 1. The unusual and very characteristic Seebeck thermoelectric data obtained from the HTSC systems have been accounted for recently on just such a resonant basis (Wilson 1997) [2], and the same situation is compatible likewise with the observed parabolic pressure behaviour of $T_c(p, P)$ (Wilson 1994) [2]. Clearly the above experiments now deserve repeating on high quality $HgBa_2CuO_{4+\delta}$.

Appendix

The following may prove useful in keeping track of the text. Remember $\Delta\mathcal{T} = -(\Delta\mathcal{R} + \Delta\mathcal{A})$. Normalized incremental effects in a probe signal χ: $\frac{\Delta\chi}{\chi} = \frac{\chi(\text{pumped}) - \chi(\text{unpumped})}{\chi(\text{unpumped})}$.

For pump generated α—i.e. hot electrons near E_F probed at picasecond delay times in probe process 1: (hot e) into $^{8}\text{Cu}^{0}_{III} \rightarrow {}^{9}\text{Cu}^{1-}_{III}$.

(all at 1.5 eV)		$\Delta\mathcal{R}/\mathcal{R}$		$\Delta\mathcal{A}/\mathcal{A}$		$\Delta\mathcal{T}/\mathcal{T}$
$T > T_c$	pump frees trapped carriers	$\uparrow$	pump pre-occupies some $^{9}\text{Cu}^{1-}_{III}$	$\downarrow$	$\therefore$	$\downarrow$
$T < T_c$	pump additionally breaks up pairs	$\Uparrow$	ditto	$\downarrow$	$\therefore$	$\Downarrow$

For pump generated β—i.e. local pair fluctuations $^{10}\text{Cu}^{2-}_{III}$:

probed at *nano*second delay times, in probe process 2: $^{10}\text{Cu}^{2-}_{III} \rightarrow$ (e at E_F) and $^{9}\text{Cu}^{1-}_{III}$.

(all at 1.5 eV)		$\Delta\mathcal{R}/\mathcal{R}$		$\Delta\mathcal{A}/\mathcal{A}$		$\Delta\mathcal{T}/\mathcal{T}$
$T > T_c$	pump freed carriers mostly retrapped	$\downarrow$	v. small number of long-lived local pairs	$\uparrow$	$\therefore$	–
$T \sim \frac{5}{6}T_c$	free carriers transferred into paired state	$\Downarrow$	individual pairs now metastable	$\Uparrow$	$\therefore$	$\Downarrow$
$\ll T_c$	by pump	$\Downarrow$	drops as individual pairs taken into condensate	$\uparrow$	$\therefore$	$\downarrow$

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