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A negative- U interpretation of the femtosecond laser pulse-induced crystallographic expansion of a cuprate HTSC material reported recently by Gedik *et al*

John A Wilson

H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

E-mail: john.a.wilson@bris.ac.uk

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Abstract

Gedik *et al* have very recently demonstrated using a pump/probe femtosecond laser technique that the c -axis lattice parameter of $\text{LaCuO}_{4+\delta}$ temporarily becomes expanded by as much as $2\frac{1}{2}\%$ following pulsed laser optical excitation at 1.55 eV. Access to an out-of-equilibrium metastable excited state is observed to develop on a timescale of 30 ps. Subsequently the latter state decays, displaying a still longer half-life of just over 300 ps. Observation of the temperature independence of this laser-induced interstate transfer and of the linear dependence of the production of the metastable population upon the energy delivered per unit area by the initiating light pulse (beyond a key threshold fluence) have been interpreted by Gedik *et al* within the framework of standard p-to-d, O-to-Cu, 'charge transfer' excitations. By contrast these same data are reinterpreted here in terms of pumped local pairs, within a negative- U scenario of cuprate HTSC behaviour long advocated by the current author. The d^8 -to- d^{10} laser-induced augmentation in the negative- U state population ($^{10}\text{Cu}_{\text{III}}^{2-}$) brings marked c -axis expansion by virtue of (i) the local electrostatic charge imbalance, (ii) the increased antibonding nature of the electron double-loading $d^{10}(p^6)$ configuration created at pair-receptive Cu_{III} coordination units, and (iii) the layered nature of the cuprate crystal structure. The new observations are related to Röhler's striking, standard crystallographic observations, to stripe domain formation and to previous pump/probe experiments.

1. Summary of the pump/probe experiment of Gedik *et al*

In an interesting alternative to the customary pump/probe, femtosecond, pulsed laser spectroscopy, Gedik *et al* [1] have recently secured very revealing new information on the ultra-fast, local electronic/structural conditions in an excited high- T_c cuprate superconductor. The material investigated was optimally doped $\text{La}_2\text{CuO}_{4+\delta}$ in thin film form, and the probe technique used was electron diffraction of the excited state structure (as against the earlier

examination of changes to the optical properties). The electron pulses employed to obtain this time-dependent diffraction information were generated by converting energy-tripled photoelectrons, produced under the initial 100 fs laser pulse, into a short wavelength electron packet via acceleration of these photoelectrons through a 30 kV potential drop. A de Broglie wavelength of 0.07 Å ensues, and this permits high-order small-angle electron diffraction data then to be acquired (in reflection) from the excited sample. Note the penetration depth for the diffracting electrons (at just 10 nm) is much less than that of the laser light (~150 nm). The $\text{La}_2\text{CuO}_{4+\delta}$ film (of thickness 50 nm) stands on a LaAlSrO_4 substrate, the latter transparent to the given laser radiation. The radiation is delivered at rather high fluences of up to 20 mJ cm^{-2} , but only at such a pulse repetition time (1 ms) as to ensure relatively little sample heating. The path difference travelled through the equipment between the light pulse and the slower electron packet is made such as to yield absolute relative time shifts between the two signal channels. The (0, 0, 10) *c*-axis spot locations were monitored in the equilibrium and out-of-equilibrium structural conditions of the sample. The diffraction patterns were recorded by use of a CCD camera sensitive to the receipt of individual electrons.

Very significant changes in the local *c*-axis lattice parameter, of as much as $2\frac{1}{2}\%$, have been discovered, far bigger than could arise simply from thermal expansion. The actual c_0 values attained within each cycle are dictated by the energy delivered to the sample per unit illuminated area by the change-initiating light pulse. The femtosecond pulses come from a 1.55 eV photon energy, Ti^{3+} :sapphire laser. This energy is, it so happens, a special one for the cuprate HTSC materials, as made apparent in previous optical pump/probe spectroscopy [2, 3] and related experimentation [4, 5]. The present activating light train is of less than one picosecond duration. Below T_c the bulk of the Cooper pairs reconstitute on a 10 ps timescale, but entry into the *c*-axis expanded, metastable condition proceeds over a somewhat longer characteristic settling-in period or ‘rise time’ with $\tau_{1/2} \approx 30 \text{ ps}$. Subsequently this expanded condition decays manifesting a very much longer characteristic half-life of just over 300 ps. Accordingly the original condition is not fully restored until after several nanoseconds. Successive laser pulses were spaced out at intervals much longer than this (1 ms), and their intensity could be modified to probe the effect upon the observed structural response of the photon dosage to have been delivered per unit illuminated area (or ‘fluence’).

One very notable outcome is that the monitored transient diffraction changes are discovered to be virtually independent of temperature up to 300 K—a feature that speaks of their primarily electronically driven form. The lattice parameters locally become very appreciably changed (*c* by up to $2\frac{1}{2}\%$) without any alteration to the crystal structure or symmetry. There is observed to arise steady transfer of diffraction weighting across an isosbestic-like point (in c^*) between the coupled initial and expanded state spot locations ((0, 0, 10) normally being the spot followed) as the metastable product of the interstate transfer excitation accumulates. The ultimate fall-back in the latter population does not exhibit such a characteristic, but would seem from its temperature independent form to involve the emission of acoustic phonons. The clear isosbestic nature to the metastable state build-up permits quantitative record of the process to be obtained through an integration of the diffraction weighting changes occurring to either side of the isosbestic point, and then time-difference diffraction profiles can be produced. The actual magnitude of the maximum spot displacement attained depends upon the total photon dosage delivered per unit illuminated area to the sample per initiating light pulse. Maximal displacement, materializing around 30 ps after the initial pulse, is found to grow linearly with the fluence employed, but this rise begins only beyond a set threshold level of 5 mJ cm^{-2} . Very interestingly the latter (rather high) threshold fluence equates (upon insertion of an absorption coefficient of $7 \times 10^{-4} \text{ cm}^{-1}$) to the delivery per pulse of 0.12 of a 1.55 eV photon per planar Cu atom. At this juncture up to one in eight of

the basal Cu–O coordination units could then have absorbed such a photon, a figure which is, note, very comparable to the ‘charge doping’ level in the measured optimally doped sample of $\text{La}_2\text{CuO}_{4+\delta}$. We shall return to this important observation in section 4. The continuous changes detected in the overall lattice parameter with the time lapsed and with the fluence delivered bring to mind isostructural alloying, and what is known there as Végard’s law behaviour, as a sample strains cell by cell to accommodate to the local atomic size distribution.

2. Summary of the negative- U interpretation of the HTSC phenomenon

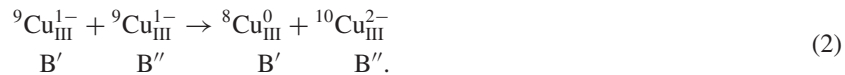
In the publication by Gedik *et al* [1] the above metastable condition is proposed to come from standard p-to-d ‘charge transfer’ electronic excitation, but quite why the latter should in that case precipitate a metastable state of such unusually long duration is not apparent to the author. Furthermore, both optical data and band structural calculation would indicate that this normal charge transfer edge (from the topmost valence-band states of dominantly $\text{O}(p_z)$ to the lowest conduction-band states of dominantly $\text{Cu}(d_{x^2-y^2})$ parentage) is not reached in the cuprates until 1.8 eV or above. What *is* encountered at somewhat lower energy in the mixed-valent cuprates are di- to trivalent inter-coordination unit charge transfers. It is, of course, electron transfers like these that confer upon the HTSC systems, essentially mixtures of the two Mott insulators La_2CuO_4 and LaCuO_3 , their mixed-valent metallicity. At a local level such inter-subsystem transfers (hops from coordination unit type A to type B) can be expressed in the notation I introduced in [6] as



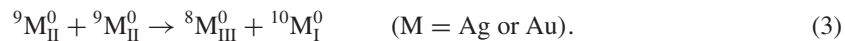
Here the Roman subscripts denote the formal, Cu(d)/O(p)-hybridized site valence, whilst the upper left numbers indicate the net complement of outer (d-symmetry) valence-band electrons instantaneously residing in the given Cu–O coordination unit. The upper right figure marks the site charge balance (0) or imbalance (for the higher valent Cu_{III} site above, the 1– of an extra electron—the ‘single loading’ of the $d_{x^2-y^2}$ symmetry σ^* -state there).

A site partaking of formal trivalence is conferred within the mixed-valent milieu by proximity to some substituent or interstitial atom. Such augmentation in Cu valency is called for to satisfy locally the requisite electron complement still demanded by the main oxygen-dominated valence-band states (as in Sr-substituted $(\text{La}/\text{Sr})_2\text{CuO}_4$), or to satisfy some increased requirement (as in interstitially super-oxygenated $\text{La}_2\text{CuO}_{4+\delta}$). Optimal doping in regard to HTSC T_c value finds 16% of the CuO array of coordination units at any one time so raised in formal valency to Cu_{III} . This local nature of the doping is very evident when using local probes such as nuclear magnetic resonance (NMR).

The above local, inter-subsystem, electron transfer excitation was revealed from the earlier spectroscopic pump–probe [2–4] and related experiments [5] to occur in sharp excitonic fashion at—by chance—virtually 1.55 eV. Moreover this earlier pump–probe work first made manifest the ensuing population of relatively long-lived states being accessed beyond the initially excited condition. What was advocated in [6] by the present author as happening is entry into metastable ‘double-loading’ at the Cu_{III} sites. One should for the above excited trivalent (B) sites consider an energetically down-hill’ two-site relaxation as being open to the hot carriers



Such a mode of attainment of the doubly loaded ‘negative- U ’ state bears echoes of the permanent site ‘disproportionation’ exhibited by *divalent* AgO, or AuO and CsAuCl_3 , where



In the latter process the crystal structure actually becomes statically transformed to set up formal M_I and M_{III} sites, these displaying changed local structural coordinations and associated Madelung energies. In the cuprates no such permanent disproportionation is directly accessible from the Mott-insulating *divalent* condition. Note that whether the disproportionation process (3) goes forward or not is dictated mainly by the degree of stability (in relation to d^9) being introduced with the $(p^6)d^{10}$ closed-shell configuration, this aided somewhat by the relative stability gained at d^8 upon adoption of four-fold square-planar coordination. What is different between the above referred to 4d/5d Ag/Au materials and the 3d cuprates is a diminished antibonding elevation for the $pd\sigma^*$ states within ‘first-series’ materials, the result of their relatively contracted d-symmetry wavefunctions. Recall in a 3d material that there are present no 2d states within the atom core with which to necessitate state orthogonality. The outcome is a disparately contracted radial expectation value for the 3d-state—a condition bringing to first-series materials their increased propensity towards Mott localization. (A comparable situation arises later on in the Periodic Table between 4f and 5f systems.) This 3d state binding contraction becomes very rapidly more pronounced, both radially and energetically, the greater the formal site valence in play. One immediate outcome with regard to the latter point is that (${}^9\text{Zn}_{III}^0$) LaZnO_3 becomes totally inaccessible, with even (${}^8\text{Cu}_{III}^0$) LaCuO_3 barely stable. Indeed it is because ${}^8\text{Cu}_{III}^0$, ${}^9\text{Zn}_{III}^0$, and beyond them ${}^{10}\text{Ga}_{III}^0$ have become so deep-lying—the latter in Ga_2O_3 and GaN falling at -18 eV—that a metastable, negative- U , ‘double-loading’ state ${}^{10}\text{Cu}_{III}^{2-}$ is ever to be attainable, bearing in mind the large Madelung potential change incurred due to its now reduced *nuclear* charge.

Process (2) discussed above would be one for producing local pairs from the optically generated excess content of ${}^9\text{Cu}_{III}^{1-}$. What about obtaining such pairs directly from ${}^9\text{Cu}_{II}^0$, the majority species in the mixed-valent, unpumped state, towards the sourcing at reduced temperatures of the system-wide superconductivity? What long ago was proposed in [6a, 6b] is the three-site, mixed-valence process



This achieves the desired product, ${}^{10}\text{Cu}_{III}^{2-}$, (and through the agency of the latter the nodal Cooper pairs) without the energetically forbidden and structurally undesirable divalent disproportionation of process (3). By virtue of the crystal structure the greater part of the carriers in HTSC materials occupy states in the axial, saddle regions of the Fermi surface. These not only have their Fermi momenta directed largely in the x and y directions, but, in consequence of the saddle geometry, their Fermi velocities too are axially directed (y and x). Residing at the shallow saddles (for the given n and E_F) these carriers are heavy and highly correlated. Indeed they become prone to weak localization promoted by the site disorder as n slips back towards unity ($p \rightarrow 0$) and the Mott-insulating, band half-filling condition is approached. These are the carriers which undergo the chronic anisotropic electron–electron scattering that characterizes the general transport properties of the HTSC condition [6d]. The boson creation process of equation (4) is seen as sitting at the heart of this strong scattering along with the ensuing electron–boson scattering. In process (4) the dominantly x - and y -directed electrons are understood as entering onto the third, *trivalent*, site in a collision (inelastic with respect to (wrt) the lattice) cum joint tunnelling process (resonant wrt E_F) to form the doubly loaded ${}^{10}\text{Cu}_{III}^{2-}$ entities. Note that, the latter pair-state is not identical to ${}^{10}\text{Cu}_I^0$, as present in copper monovalent Cu_2O or KCuO —hence the usage of our expanded notation. Clearly ${}^{10}\text{Cu}_{III}^{2-}$ is to be expected to reside at a somewhat greater absolute binding energy than ${}^{10}\text{Cu}_I^0$ due to its local trivalent Madelung potential and contracted ion radius. Indeed in figure 1 of [7], I positioned the ${}^{10}\text{Cu}_{III}^{2-}$ state to reside in close resonance with the Fermi energy, as the latter comes to be established within the mixed-valent $\text{Cu}_{II}/\text{Cu}_{III}$ oxide. This Feshbach-like

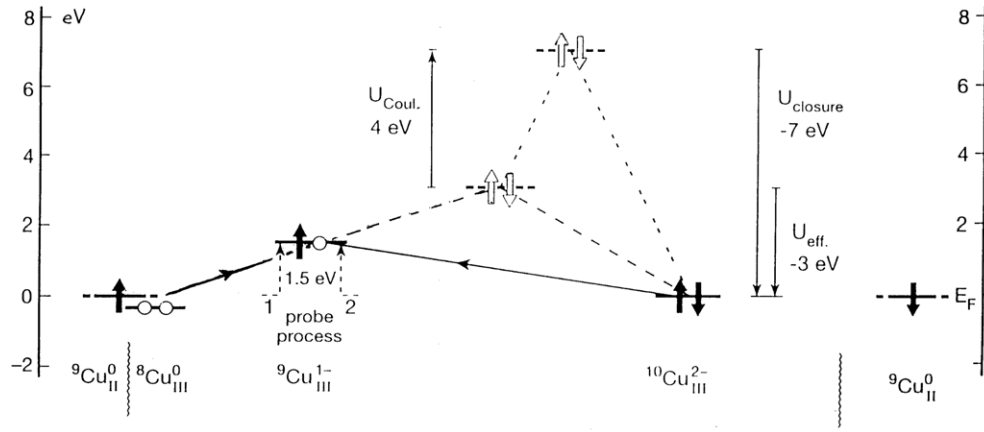


Figure 1. The resonant negative- U model from [9]. The symbols indicate a local coordination unit's nominal cation valence along with its instantaneous charge loading, both current and as deviation from the norm. The figure indicates the fluctuational state-loading energies for the trivalent ('doped') site loading sequence ${}^8\text{Cu}_{\text{III}}^0$, ${}^9\text{Cu}_{\text{III}}^{1-}$, ${}^{10}\text{Cu}_{\text{III}}^{2-}$ to be a re-entrant one. This is due to the shell closure at p^6d^{10} and accompanying collapse in σ/σ^* p/d interactions. Because of some permanent, metallizing, charge transfer between the two subsystems in the mixed-valent ground state, ${}^9\text{Cu}_{\text{II}}^0$ and ${}^8\text{Cu}_{\text{III}}^0$ are effectively brought to a common Fermi energy. In optimally doped HTSC systems the negative- U double-loading fluctuational condition ${}^{10}\text{Cu}_{\text{III}}^{2-}$ becomes stationed in near-resonance with E_F . This makes U_{eff} (per electron) = -1.5 eV, in keeping with the value extracted from the femtosecond laser pump-probe optical experiments [2, 3]. Note the customary definition of U is $(E_{n+2} - E_{n+1}) - (E_{n+1} - E_n) = [E_{n+2} + E_n] - 2E_{n+1}$, which in the present case gives $U = [E(d^{10}) + E(d^8)] - 2E(d^9)$, and where note $U = U_{\text{effective}} = U_{\text{Coulombic}} - U_{\text{shell closure}}$. Given $U_{\text{Coul}} = +3$ eV, and with $U_{\text{shell closure}} = -6$ eV, we reach $U_{\text{eff}} = -3$ eV per pair or -1.5 eV per electron, the value supported by the experiments of [2-5].

resonant stationing of the 'negative- U ' double-loading entity is analogous to what presently is being met with in the ultra-low temperature, gaseous, trapped atom/molecule systems, with their effective energy degeneracy between the fermionic and bosonic components to the overall system.

The BCS/BEC, mixed system, crossover modelling of the HTSC phenomenon has long been addressed in certain theoretical works [8], but without ever examining too closely the sourcing of such a circumstance, or taking on board the mixed-valent, inhomogeneous nature of the situation. From a consideration of Stevens *et al*'s optical pump/probe data [2], first in [7] and then subsequently in [9-14] (following upon the kinetic induction work of Li *et al* [4], the infra-red thermomodulation work of Little *et al* [5] and further pump/probe laser work from Demsar *et al* [3]), identification was adduced of the negative- U energy for the metastable Cu_{III} based condition as being -1.5 eV per electron (or -3.0 eV per pair—as customarily this quantity is specified). As indicated above, such a value would see ${}^{10}\text{Cu}_{\text{III}}^{2-}$ being, by chance, stationed at the same absolute energy as ${}^8\text{Cu}_{\text{III}}^0$, this latter in unison with ${}^9\text{Cu}_{\text{II}}^0$ setting up the Fermi level in the mixed-valent metal. The overall situation is as summarized in figure 1 (redrawn slightly from [7] as in [9]).

The kinetic induction work of Li *et al* [4] proved to be especially valuable in coming to the above identification. This particular technique deals specifically with the superconductive behaviour and with the breakage of pairs. The laser which Li *et al* employed was tunable between 1.45 and 1.65 eV, and this flexibility permitted a clear resolution of the excitonic nature to the main feature to be obtained centred upon 1.54 eV. Very significantly, it also enabled the detection of a pair of satellite features, one lying to either side of the principal excitation

and showing very pronounced and distinctive temperature dependencies. The energies of the satellites are most revealing, standing in YBCO₇ at 41 meV to the low energy side and at 70 meV to the high energy side of the central peak. In [4] Li *et al* attempt to relate the above events again to ‘charge transfer’ excitation, but in section 3 of [10] I returned once more to a negative- U based interpretation of these observations. There the 41 meV satellite was deemed attributable to a local pair breaking that in this case is assisted by a spin-flip (singlet \rightarrow triplet) energy contribution drawn from the reservoir of Cooper pair states during the negative- U pair disruption process



Appropriately this 41 meV satellite peak fades away as the temperature is elevated somewhat beyond T_c , mirroring here what is to be seen in neutron spin scattering—taken to track directly the singlet \rightarrow triplet Cooper pair excitation [15]. The higher energy satellite is, by contrast, adjudged to be associated with the production of an optic phonon during the course of local pair disruption. The latter satellite becomes more pronounced this time as the temperature is raised. Its energy shift of 70 meV points to the Jahn–Teller extended Cu–O bond c -axis phonon as being the one involved here. As was noted in [10], that particular phonon mode is strongly in evidence in IR work in spite of the system being a metal. Why in particular this c -axis bond should become coupled with process (5) is that the excitation product ${}^9\text{Cu}_{\text{III}}^{1-}$ holds a Jahn–Teller active configuration.

3. The engagement of the lattice in HTSC events

The above is very definitely not the only point at which one discovers phonons—or, at a local level, the lattice—becoming enmeshed in HTSC phenomena. Indeed many phonons exhibit sharp changes at T_c , as manifest in IR and particularly Raman experiments [16]. Moreover, techniques like EXAFS and PDF [17, 18] directly register marked changes to the Cu–O bond lengths at T_c . Then again we encounter the now infamous 50–70 meV ‘kinks’ in the ARPES band dispersion data, about which so much has recently been written [19–21]. In [11, 13] I have discussed the latter extensively within the present negative- U scenario, in terms of the local pair controlled condensate supporting a plasmon mode of A_{1g} symmetry at such an energy. This mode is able to couple, then, with the topmost optic phonon, which this time relates to the *basal* Cu–O bonds. A strong dynamic coupling of the above local-pair-governed mode with the Σ_1 branch from the Γ -point B_{2g} phonon is very much in evidence in the neutron scattering derived, phonon dispersion curves towards the zone boundary [22]. Perhaps still more revealing, and now highly relevant to our understanding of the new findings reported by Gedik *et al* [1], are the direct and very accurate lattice parameter determinations put together fairly recently by Röhler [23] from right across several entire series of systematically doped HTSC systems.

What the Röhler data plots make manifest is that within the central range of HTSC-inducing dopings (i.e. from $p = 0.10$ through to 0.22) the *basal* lattice parameters are significantly enlarged as compared with what one might expect were the measurements simply to follow a smooth decrease from ${}^9\text{Cu}_{\text{II}}^0$ to ${}^8\text{Cu}_{\text{III}}^0$, attributable to the increase in valence and the diminished number of antibonding electrons. The detected enlargement is found to be greatest at $p = 0.16$, precisely where T_c maximizes, and it is, furthermore, larger for those systems for which T_c^{max} is higher. The magnitude of this finding (recorded, it must be noted, up at 300 K) is around $\frac{1}{2}\%$ in a_0 . This has to be compared with the enlargements of up to $2\frac{1}{2}\%$ in c_0 witnessed now by Gedik *et al* (including at 300 K). In the prevailing resonant conditions of the *unpumped* circumstance, the metastable ${}^{10}\text{Cu}_{\text{III}}^{2-}$ negative- U state population, to which the effect has been attributed in section 2 of [12], may be expected to be appreciably smaller, and it is from this

base that the $^{10}\text{Cu}_{\text{III}}^{2-}$ population then temporarily becomes built-up further during relaxation from the laser pumping. As noted at the outset, the large size of the $^{10}\text{Cu}_{\text{III}}^{2-}$ entity arises from its internal charge imbalance, assisted by the fact that all the $\text{pd}\sigma^*$ antibonding states have now become occupied. In [1], Gedik *et al* introduce a lattice energy calculation based on their interpretive notion of a p-to-d ‘charge transfer’ excitation to access $(\text{p}^5)^{10}\text{Cu}_{\text{II}}^{1-}$ (often written briefly as Ld^{10}). They demonstrate that the rate at which the lattice parameter is observed to swell with the photon fluence delivered by a given laser pulse is precisely as follows from employing simple electrostatics. However, note that this same agreement would extend to our current negative- U modelling, given the appearance of just half as many excited centres but these now bearing double the electronic charge. It should be restated here that Gedik *et al* have concentrated upon the c -axis changes they are inducing, whilst Röhler, so as to avoid potential complications with Jahn–Teller effects and other structural detail, focused upon the ab basal areas. In consequence of the c -axis softness of the present layered structures, some fraction of the above difference present between basal and c -axis percentage changes inevitably is going to reflect this distinction.

4. Towards a full understanding of the data from Gedik *et al*

It is well at this juncture to be aware too of an important distinction between Gedik *et al*’s current pump/probe experiment and the earlier spectroscopic pump/probe work from Stevens *et al* [2]. There the electrons were pumped by the Ti^{3+} :sapphire laser not using the fundamental emission line, but its second harmonic, of photon energy 3.1 eV. After such excitation the $^{10}\text{Cu}_{\text{III}}^{2-}$ metastable population builds appreciably more rapidly under phonon- and electron-assisted trickle-down from the higher energy. With the Gedik arrangement, where the fundamental is employed, there is, by contrast, barely sufficient energy to reach the energy bar set by $^9\text{Cu}_{\text{III}}^{1-}$ for any ready advancement over into the doubly loaded negative- U condition. Gedik *et al* accordingly experience a sizeable ‘rise time’ of the order of 100 ps for the metastable expansion to plateau out, prior to its subsequent and yet slower nanosecond decline.

While this ‘rise time’ in the appearance of the pumped metastable condition is readily understandable, the reason for the observed fluence threshold regarding the structural modification demands more consideration. First, remember that what the above experiment records is not the population change *per se*, but the lattice parameter change in response to that population change. If some new metastable population can be accommodated within precisely the same structural framework as a base population, whether natural or laser-induced, there is no lattice parameter change to record. The framework within which the $^{10}\text{Cu}_{\text{III}}^{2-}$ materialize in post-pumped $\text{La}_2\text{CuO}_{4+\delta}$ is anticipated to be much like the ‘stripe structure’ existing in LBCO and LSCO. If the present author is correct in regard to the latter, the valence ordering structure acquired there actually takes $2\text{-}\mathbf{q}$ diagonal form [12] and not the $1\text{-}\mathbf{q}$ geometry invariably portrayed. The fact that the recent spin-polarized neutron diffraction data from Christensen *et al* [24] will indeed support the $2\text{-}\mathbf{q}$ (spin) structuring advocated in [12] has very recently been attested to by Fine [25]. The $2\text{-}\mathbf{q}$ charge stripe structure in [12] is of alternating $^8\text{Cu}_{\text{III}}^0$ and $^9\text{Cu}_{\text{II}}^0$ sites defining strings—the ‘rivers of charge’—these bounding diagonal square domains of the less metallic, more magnetic, majority species, $^9\text{Cu}_{\text{II}}^0$. Within this structural order the most likely creation and dwelling spot for the $^{10}\text{Cu}_{\text{III}}^{2-}$ double-loading, whether spontaneous (persuant upon the above elaborated resonance) or laser-induced, falls at the stripe crossing-points where the Madelung potential becomes greatest. Stripe formation is observed to be best organized at the sub-optimal hole content of $p = 1/8$, and at that stage there arise two stripe crossing-points within each $8 a_0$ supercell (see [12]—figure 1). By the $p = 0.155$ of optimal doping (in respect of T_c , although not the condensation energy) both these sites will take on the

additional holes (i.e. have become ${}^8\text{Cu}_{\text{III}}$) (see [12]—figure 4), provided, that is, one stays with the $8 a_0$ supercell—which is what the diffraction results would indicate for this composition.

Now, of the threshold photon fluence (when each of the 64 copper centres within this cell has been delivered one eighth of a photon) only that fraction taken up around the ${}^8\text{Cu}_{\text{III}}^0$ centres in the stripes is able to engender the appearance of an excited ${}^9\text{Cu}_{\text{III}}^{1-}$. This could well mean, then, the production of only one such entity per cell. Only for fluences greater than this may the disproportionation/collisional process of equation (2) be able to secure in additive fashion the appearance of new *doubly-loaded* ${}^{10}\text{Cu}_{\text{III}}^{2-}$. The added fluence now witnesses this laser-induced population advance steadily. What such build-up in the ${}^{10}\text{Cu}_{\text{III}}^{2-}$ population (beyond that naturally present through process (4)) will mean for the superconducting properties of the system is an important issue to examine. It is not a foregone conclusion as to whether the additional local pairs induced by laser pumping are going actually to increase or to decrease T_c . Recall, in the present resonant circumstances of the negative- U modelling considered, there is delicate interplay between the local pairs and the sustained Cooper pairs. It is presumed that the absence of structural change prior to the emergence of the extra ${}^{10}\text{Cu}_{\text{III}}^{2-}$ content comes as a result of there being negligible alteration to the lattice conditions across process (1), the means wherewith the feed stock of ${}^9\text{Cu}_{\text{III}}^{1-}$ is procured: remember *both* ${}^9\text{Cu}_{\text{II}}^0$ and ${}^9\text{Cu}_{\text{III}}^{1-}$ are Jahn–Teller active.

The likely outcome is that the added ${}^{10}\text{Cu}_{\text{III}}^{2-}$ emerging under process (2) will become deleterious to the superconducting performance if and when they should become heavily relaxed onto the lattice to impede thereby the free exchange of paired electrons with the sustained electronic environs. This is to say not only do the binding energies of the negative- U pairs and the propagated Cooper pairs have to be quite similar, but so too must the geometric lattice environments in which the two interchanging varieties of pair find themselves based. If the local pairs are given the opportunity to relax too strongly onto the lattice, let alone segregate, this will impair not only the superconductivity but the basic conductivity of the mixed-valent system as well. It is the comparable problem in regard to heavy polaronic and then bipolaronic behaviour [26] that weighs heavily against a purely lattice-mediated sourcing of HTSC, as compared with the present dominantly electronic scenario.

5. The support offered by further recent experiments to the above interpretation

A clear expression of what is happening in the Gedik experiment is afforded by the pump/probe spectroscopic data published a little while ago by Kusar *et al* [3] on LSCO, a study in which considerably lower laser light fluences were used. Working from the superconducting state, the latter group tracked the rise and subsequent relaxation of the excitation products by means of the changes incurred to the reflectivity at 1.5 eV. As a result of the very different rise and recovery behaviour for the component signals as a function of time, temperature and doping level, it proved possible to distinguish three very different channels to the relaxation. Primarily one senses recovery in the Cooper pair population, characterized by a relatively slow bottle-neck, phonon-controlled, disruption and restitution—the actions of which all terminate of course at T_c . Next there are in evidence the much more rapid changes to a further very substantial portion of the recovery signal. These one is able to link with the local pairs by their association with a T^* , which lies well in excess of T_c , and a $\Delta^*(T)$ that likewise is well in excess of $\Delta_c(T)$. Interestingly both latter gaps emerge from the analysis as relating specifically to the maximal d-wave values along the saddle, gap-antinodal, directions. Finally, as well as these two preceding components, a third relaxation product has long been recognized [2, 3], showing an even longer relaxation period of nano- if not microsecond duration. It is this third component which the much higher irradiation fluences employed by Gedik *et al* would look to be promoting. The emergence of a great many ${}^{10}\text{Cu}_{\text{III}}^{2-}$ entities, far in excess of their natural equilibrium level,

would appear to have led to enhanced self-trapping of these products. It is the local structural expansion of such temporary accumulations of $^{10}\text{Cu}_{\text{III}}^{2-}$ that one seems to be detecting in the Gedik experiment.

The above form of interpretation would stand in line with what at equilibrium has been reported within samples of steadily decreasing doping. Under the latter less metallicized, more ionic circumstances, as the Cu_{III} centres take on greater local definition, the effect is to adjust the negative- U level to somewhat greater binding energy, \mathcal{U} . This will diminish the electron-pair transfer rate between the Cu_{II} and Cu_{III} subsystems: as Δ^* rises, Δ_c falls [14]. The scanning tunnelling microscopy images very recently published by Gomez and colleagues [27] once more have very graphically illustrated the inhomogeneous nature of the instigating pairing. Those inhomogeneous environments, in BSCCO largely statistical in form, include both optimally disposed and pair-localizing regions. The latter localities grow in degree and extent with underdoping—and now, it would appear too, with strong laser pumping as well. The production of such lattice expanded nanoregions is found in the pump/probe work to be virtually temperature invariant, but their temporary effect upon T_c could well be very substantial, a matter that one now should try to determine.

With regard to matters dealing with pump/probe work and the negative- U interpretation of HTSC, attention finally is directed to a very recent paper from Kaindl *et al* [28]. There the spectroscopic probe employed lies not in the electron volt but the milli electron volt range; i.e. in the 1–2 THz range. By ascertaining the changes to $\sigma_1(\omega)$ and $\sigma_2(\omega)$ at such energies arising from the 1.5 eV laser pumping, Kaindl *et al* demonstrate, with the aid of a two-fluid model, taken in conjunction with the Rothwarf–Taylor rate equation for the relaxation, that the latter actually is dominated within the main 3–30 ps range by the term *quadratic* in n^* , the photo-excited, freed quasi-particle density. This observation would endorse that the route to the rapid re-establishment of pairing does indeed proceed, then, in a bimolecular fashion as expressed above in equations (2) and (4), and that entail, of course, the appearance of the electronic negative- U state $^{10}\text{Cu}_{\text{III}}^{2-}$.

We have reached accordingly a very feasible model with which to comprehend each point being presented by Gedik and colleagues in their most valuable of additions to HTSC phenomenology. It will be extremely interesting now to see whether those advocating spin fluctuation and phonon scenarios for HTSC find themselves in a position to address these striking new results.

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Note added in proof. The extra optical absorption around 1.5 eV involves primarily d-to-d rather than p-to-d intersite excitation. Such d–d excitation is weak, being optically forbidden, but is enhanced in L-edge RIXS (resonant inelastic x-ray scattering) data. A recent assessment of the detailed form of the absorption edge in pure La_2CuO_4 has very recently been made by D S Ellis and co-workers following improved resolution K-edge RIXS work (arXiv: 0709.1705 [cond-mat.str-el]). Intervalence excitation is of course absent here. p-to-d charge transfer is placed near 2 eV.

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