Possible Origin of Preformed Hole Pairs and Superconductivity in Cuprates

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This paper addresses the long standing and controversial issue of the origin of superconductivity in cuprates. It is shown that the superconductivity can be attributed to amphoteric defects associated with vacancy sites in copper oxide planes. A local defect lattice relaxation results in a negative-$U$ energy binding two holes on amphoteric defects in the donor configuration that act as preformed boson pair. Thermodynamic equilibrium between defects in the donor and acceptor configurations stabilizes Fermi energy at the amphoteric defect charge transition state assuring resonant coupling between free holes and the localized hole pairs. Model calculations provide explanation for most important superconducting properties of cuprates. They show that the critical temperature is primarily determined by the density of the amphoteric defects in the donor configuration. This explains ubiquity of dome-like dependence of the critical temperature on the doping as well as its universal dependence on the superfluid density. Intentional doping with chemical acceptors or donors is neither necessary nor sufficient condition for superconductivity that is fully determined by the amphoteric defects whose concentration can be controlled by crystal nonstoichiometry. The only role of chemical doping is changing the balance between concentrations of amphoteric defects in the donor and acceptor configurations resulting in an increase of the superfluid density and thus also the critical temperature for acceptor and a decrease for donor doping. This accounts for the experimentally observed distinct asymmetry between the dome structures for the chemical doping with acceptors and donors. The unusual sensitivity of the critical temperature to external perturbations is explained by the resonant nature of the coupling between free holes and preformed hole pairs. The work has broader implications as it could be applicable to other superconductors with dome-like dependence of the critical temperature on doping.
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I. INTRODUCTION

The discovery of high temperature superconductivity in cuprates (cupreous oxides) was immediately followed by explosive research that unearthed a large number of materials with critical temperatures as high as 133 K at ambient and even higher at high hydrostatic pressures. This unprecedented triumph of empirical material science created a difficult challenge for existing theories of superconductivity and despite of more than 35 years of research there is still no generally accepted explanation of the origin of the superconductivity in these materials. Although there were some indications of possible role of lattice vibrations, an absence of consistent isotope shift strongly indicated an electronic origin of the superconductivity. Initially a considerable attention was devoted to the model of resonating valence band (RVB) that was able to address some of unique features of the normal state of cuprates. Separately it was suggested that the hole pairing and superconductivity could originate from antiferromagnetic spin fluctuations. Also, several research groups have pursued theories based on quantum critical point (QCP) concept where it is argued that the properties of the material are determined by a hidden competing order parameter.

Another broad class of models of superconductivity invoked the original concept of preformed bosons in which superconductivity originates from interaction of free charge carriers with preformed pairs of charges. Different variations of this concept were actively pursued by several research groups and theoretical formalisms have been developed to understand superconductivity in various unconventional superconductors including superconducting cuprates. The main difficulty with these approaches was that they could not identify a physical process for formation of well-developed, robust negative-\(U\) centers. In addition they required for the Fermi energy to be in close resonance with the charge transition state of the negative-\(U\) centers. It was not clear how these demanding conditions could be so readily satisfied in such large variety of the high \(T_c\) cuprates.

Over more than three decades the expansive experimental and theoretical research on superconducting cuprates was summarized in many comprehensive review articles which demonstrate that there is a general consensus on several well-understood key properties common to these materials. Thus, superconducting cuprates crystalize in a basic perovskite-like structure. The parent undoped stoichiometric compounds are antiferromagnetic charge transfer insulators with a large energy gap between fully occupied charge transfer band (CBT) and empty upper Hubbard band (UHB). Charge carriers can be introduced and electrical properties can be changed by varying...
crystal stoichiometry (Cu/O ratio) and by chemical doping of the charge reservoir building blocks. The electrical properties of the cuprates are highly anisotropic with the conductivity confined to 2-dimensional CuO$_2$ planes.

In contrast, there is no common explanation or understanding of a variety of experimental observations related to the superconductivity:

1) Optimization of superconducting properties require material processing steps involving high temperature annealing and cooling under specific, well controlled oxygen ambient conditions.

2) The superconducting transition temperature shows a dome-like dependence on doping.

3) Intentional chemical p-type doping augments whereas n-type doping diminishes superconducting properties.

4) Critical temperatures for different cuprates show a universal dependence on the superconducting condensate or superfluid density.

5) Critical temperatures are strongly dependent on external perturbations: hydrostatic pressure and electrical bias.

In this paper we show that superconductivity in cuprates can be well described by an amphoteric defect model in which vacancy like defects in CuO$_2$ planes are negative-$U$ centers that can undergo a transformation between acceptor and donor configuration. The defects in the donor configuration act as localized hole pairs. The boson field of the randomly distributed pairs induces hole superconductivity at low temperature. The paper is organized in several sections that address different aspects of the superconducting properties of cuprates. In section II we briefly introduce the concept of negative-$U$ amphoteric defects that has been originally developed for semiconducting materials. An extension of the model to the case of superconducting cuprates with amphoteric defects located in 2-dimensional CuO$_2$ planes is presented in section III. The key results of the paper are presented in section IV where it is shown how coupling of free holes to pairs of holes localized on amphoteric defects in the donor configuration leads to high temperature superconductivity. It also shows how the increased doping leads to a reduction of the preformed pairs and termination of the critical temperature and high defect concentration providing a straightforward explanation for the origin of the dome like dependence of the critical temperature on the doping.
The effects of the chemical doping on the critical temperature are discussed in section V where it is shown that in both cases the superconductivity is associated with free holes in the partially occupied charge transfer band. Calculations account very well for the asymmetry in the shape of the superconducting dome observed in n-type and p-type doped cuprates. Section VI deals with the effects of external perturbations such as hydrostatic pressure and external electric field bias on the superconducting properties. Finally, section VII summarizes the results of the paper and offers an outlook on possible applications of the amphoteric defect model to other unconventional superconductors.

II. AMPHOTERIC DEFECTS AND LOCALIZED NEGATIVE-\(U\) CENTERS

There are several unique features of cuprates that distinguish them from classical superconductors. Most notably these materials do not exhibit standard metallic behavior but rather show semiconducting properties where the conductivities and carrier concentrations can be modified and controlled by intentional chemical doping with acceptors or donors and/or by varying crystal stoichiometry. Also, in a striking similarity to semiconductors whose properties are sensitive to external perturbations properties of superconducting cuprates, including the critical temperature were found to be very sensitive to hydrostatic pressure\(^{21}\) and electrical bias of thin films.\(^{22,23}\) This is strongly suggestive that physical concepts well developed and commonly used in semiconductors could provide a guidance to understanding properties of cuprates.

Localized negative-\(U\) centers i.e., centers with a negative effective electrostatic interaction energy between two electrons or two holes are well known and have been extensively studied in semiconductors. In most instances the electrostatic repulsion is overcome by large attractive potentials associated with local lattice relaxation effects. Negative-\(U\) centers have been invoked in explanation of a variety of effects observed in semiconductors.\(^{24,26}\) Notably properties of the extensively studied DX centers were explained by a negative-\(U\) behavior of substitutional donors in GaAs.\(^{27}\) Independently it was shown that vacancy-like defects exhibit negative-\(U\) behavior as they undergo transformation between negatively charged acceptor-like and positively charged donor-like configuration.\(^{28}\) The actual configuration depends on the Fermi energy and, for example, in GaAs a negatively charged gallium vacancy \(V_{Ga}\) acceptor is stable in n-type material but relaxes to a positively charged \((V_{As}+As_{Ga})\) donor complex configuration in p-type material.\(^{28}\) The transformation between these two configurations occurs at the Fermi energy at which the formation
energy of a negatively charged acceptor equals the formation energy of positively charged donor.

The amphoteric nature of dangling bond defects leads to the well-known effect of the defect induced stabilization of the Fermi energy\textsuperscript{29,31} where it was demonstrated that in semiconductors the stabilization energy, $E_{FS}$, remains constant and is located at about 4.9 eV below the vacuum level.\textsuperscript{31} The same phenomenon has been shown to account for the pinning of the Fermi energy on semiconductor surfaces and at metal/semiconductor interfaces.\textsuperscript{29} Also it has provided a universal explanation for large diversity in the doping properties of semiconductors.\textsuperscript{32} Most recently the amphoteric defect model was used to understand the unique properties of hybrid organic-inorganic perovskites and to develop a new mechanism of a dynamic doping and p/n junction formation in these materials.\textsuperscript{33–35}

In a presence of vacancy-like native amphoteric defects, the electrical properties of a semiconductor material are determined by the location of the Fermi level stabilization energy $E_{FS}$ relative to the edges of the bands of extended states.\textsuperscript{31,32} In standard semiconductors the valence band and the conduction band edges originate from orbitals of the component atoms. This results in large variations of the electron affinity and/or ionization energy and thus also band offsets between different materials. Consequently, as is illustrated in Fig. 1, this leads to large variations of the locations of semiconductor band edges relative to the $E_{FS}$ that remains constant at about 4.9 eV below the vacuum level for all materials.

Figure 1 illustrates three different examples of how the locations of the extended band edges relative to the $E_{FS}$ determine electrical properties of semiconductors in presence of amphoteric defects (ADs). Thus, as is shown in Fig. 1 (a) for the $E_{FS}$ located in the band gap the material is semi-insulating with equal concentration of the amphoteric defects in the donor and acceptor configuration. This is the case of most standard semiconductors such as e.g., GaAs and ZnSe or GaN. However, as is seen in Fig. 1(b) for high electron affinity semiconductors such as InN or CdO $E_{FS}$ pins the Fermi energy in the conduction band making these materials n-type conducting with majority of ADs in the donor configuration. Indeed, these two semiconductors are well known to show large intrinsic n-type conductivities with electron concentrations reaching mid $10^{20}$ cm$^{-3}$ range.\textsuperscript{36,37} On the opposite side materials with low ionization energy in which $E_{FS}$ falls into the valence band are intrinsically p-type conducting. For example, in the case of SnTe majority of ADs are in the acceptor configuration and pin $E_{FS}$ at about 0.5 eV below the valence band edge stabilizing the free hole concentration at $3 \times 10^{21}$ cm$^{-3}$.\textsuperscript{38}

In superconducting cuprates, the band gap originates from the metal-insulator transition that
FIG. 1. (a), (b) and (c) Examples of possible three different locations of the conduction band (CB) and the valence band (VB) relative to $E_{FS}$ located at 4.9 eV below the vacuum level. (d) dependence of the formation energies of amphoteric defects (ADs) in the donor and acceptor configuration on the Fermi energy. The effective negative energy $-U$ binds two holes on an amphoteric defect in the donor configuration.

splits a partially filled d-band of Cu into fully occupied charge transfer band (CTB) separated from an empty upper Hubbard band (UHB) by large charge transfer gap of 1.5 to 2 eV. Despite different origin of the band gap, incorporation of acceptor-like (donor-like) defects contributes free holes (electrons) to the CTB (UHB) the same way as in semiconductors. As will be seen later the situation encountered in superconducting cuprates corresponds the case depicted in Fig. 1 (c) where the $E_{FS}$ is located in the charge transfer band (CTB) with majority of ADs in the acceptor configuration producing conducting free holes in CuO$_2$ planes.

III. AMPHOTERIC DEFECTS IN CUPRATES

In general, the electrical properties of non-metallic materials at elevated temperatures are determined by the intrinsic concentrations of free carriers thermally excited over a band gap, chemical doping and the concentration of electrically active lattice defects. Because of the large energy
gap between CTB and UHB, we assume that the intrinsic carrier concentrations can be safely ignored at the annealing or thermal processing temperatures typically used to optimize superconducting properties of cuprates. Consequently, the conductivity of cuprates is fully determined by crystal lattice defects and/or by intentional chemical doping. Chemical doping was used to synthesize superconducting La$_{2-x}$Ba$_x$CuO$_4$ compound where divalent Ba atoms partially replacing trivalent La act as acceptors providing holes to the CTB of the CuO$_2$ planes. On the other hand, in the case of YBa$_2$CuO$_{6+\delta}$ the holes originate from nonstoichiometry associated with the excess of O, $\delta$. It is important to note that in both instances an optimization of the critical temperature required an elaborate processing of the samples at elevated temperatures with controlled ambient indicating that the superconducting properties of the samples are determined by a balance between chemical dopants and intrinsic defects at processing temperatures.

Guided by the extensive experience with amphoteric defects in semiconductors and taking into account that CuO$_2$ planes are the only irreplaceable components of all cuprate superconductors it is reasonable to assume that the amphoteric defects in cuprates are associated with the ionic Cu-O bonds. These bonds are primarily formed out of Cu $d_{x^2−y^2}$ and O $p_{x,y}$ orbitals. A removal of highly electronegative O (metallic Cu) atom from crystal lattice produces O (Cu) vacancy with the dangling bonds of Cu (O) acting as a donor (acceptor) with highly spatially localized bound electron (hole). The total energy of such localized defect is a sum of the electronic energy and the lattice energy associated with relaxation of the neighboring atoms. Therefore, the local lattice configuration depends on the charge state of the defect which, in turn, is determined by the location of its charge transition state relative to the Fermi energy.

The strong coupling between electronic and lattice degrees of freedom drives the transformation between donor and acceptor configurations and defines the amphoteric nature of the dangling bond defects. Thus, as is schematically illustrated in Fig. 2 (b) an O vacancy (V$_O$) is a donor with an electron bound in the dangling bonds of Cu. The formation energy of the ionized charged donor defect increases with increasing Fermi energy and is given by $E_{fD}(E_F) = E_{fD}(0) − [E_D(0/+ − E_F]$), where $E_{fD}(0)$ is the formation energy of the neutral donor and $E_D(0/+)$ is the energy of the donor charge transition state (Fig. 3 (d)). At high enough Fermi energy the defect can lower its total energy by, shown in Fig. 2(a), local bond restructuring in which a neighboring Cu atom moves towards the O vacant site forming (CuO+V$_{Cu}$) acceptor defect complex with a hole bound on the O dangling bonds and with the formation energy given by $E_{fA}(E_F) = E_{fA}(0) − [E_F − E_A(−/0)]$, where $E_{fA}(E_F)$ is the formation energy of the neutral acceptor and $E_A(−/0)$ is the energy of the
FIG. 2. Schematic representation of the bond breaking atom relocation associated with the transformation of an amphoteric defect between neutral donor \((V_0)^0\) (b) and acceptor \((V_{Cu}+CuO)^0\) (a) configuration. (c) defect energy dependence on the atom configuration coordinate with an energy barrier \(E_b\). (d) dependence of the amphoteric defects formation energy on the Fermi energy. The minimum of the total energy is achieved for the Fermi energy equal to \(E_{AD}(+/−)\).

Absence of any other constraints the thermodynamic minimum energy of such defect system is achieved when the formation energies of the defects in the acceptor and donor configurations are equal, \(E_{fA}(E_F) = E_{fD}(E_F)\) i.e. when the Fermi energy is stabilized at \(E_F = E_{FS} = E_{AD}(+/−) = [E_{fA}(0) − E_{fD}(0) − E_{A}(−/0) + E_{D}(0/+)]/2\). In the following, for simplicity we assume \(E_{fA}(0) = E_{fD}(0)\) which gives \(E_F = E_{FS} = E_{AD}(+/−) = [E_{D}(0/+) − E_{A}(−/0)]/2\). In general, it is expected that as is shown in Fig. 2(c) the bond rearranging transformation between neutral states of the donor and acceptor configuration requires surmounting an energy barrier, \(E_b\). The barrier plays an important role as it determines the temperature and annealing time needed to reach a thermal equilibrium for ADs and to optimize superconducting properties. Also, it can be a critical factor affecting the long-term stability of the material at room temperature.

The described above Fermi energy-controlled transformation of the dangling Cu bonds of a \(V_0\) donor into dangling O bonds of \((CuO+V_{Cu})\) acceptor applies to an analogous amphoteric defects system where the dangling O bonds of \(V_{Cu}\) acceptor undergo the Fermi energy driven transforma-
tion into dangling Cu bonds of \((O_{\text{Cu}}+V_O)\) donor defect complex. This again leads to Fermi level driven transformation between donor and acceptor configuration stabilizing the Fermi energy at the charge transition state \(E_{\text{AD}}(+/−)\). It needs to be emphasized that this thermodynamically driven equilibrium between free carriers and localized defects is the central concept of our model of superconductivity in cuprates.

In principle, the stabilization of the Fermi energy can be achieved in a stoichiometric material by annealing at a high temperature when the thermal equilibrium concentrations of vacancies on Cu and O sites are large enough to stabilize the Fermi energy at \(E_{\text{AD}}(+/−)\). Such high temperature thermodynamic equilibrium can then be frozen by a rapid cooling to low temperatures at which the defects cannot undergo the configurational transformations. Therefore, nonstoichiometry measured by excess or deficiency of O is not a unique determinant of the carrier concentration or the concentration of ADs in the donor or acceptor configuration and cannot be used to evaluate electrical properties of the material. However, the stabilization of the Fermi level is greatly facilitated in nonstoichiometric compounds with O or Cu deficiency that has to be accommodated by an increase in the concentration of ADs. This is equivalent to a reduction of the formation energy of neutral ADs, \(E_{fA}(0) = E_{fD}(0)\) (see Fig. 2 (d)).

As was discussed in the preceding section the electrical properties of an ADs containing material are determined by the location of \(E_{\text{FS}} = E_{\text{AD}}(+/−)\) relative to the fully occupied valence band or CTB and empty conduction band or UHB. In superconducting cuprates \(E_{\text{FS}}\) is located below CTB edge leading to the charge balance condition \(N_{A−} = p + N_{D+}\) where \(N_{A−} (N_{D+})\) is the concentrations of negatively (positively) charged ADs in the acceptor (donor) configuration, \(p\) is the concentration of free holes in the CTB and \(N_{\text{AD}} = N_{A−} + N_{D+}\) is the concentration of the amphoteric defects (ADs). Effects of chemical doping with either acceptors or donors can be easily incorporated in this picture and will be discussed in section V of the paper.

IV. GENERIC NONSTOICHIOMETRIC CUPRATE SUPERCONDUCTOR

The conceptually simplest and the most illuminating cases of high \(T_c\) cuprate superconductors are represented by compounds such as YBa\(_2\)CuO\(_6+\delta\) [10] or Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) [11] in which there is no intentional chemical doping and the concentration of conducting holes and the superconducting properties are entirely determined by the deviation of the O content \(\delta\), or \(\chi\) from the composition of the parent stoichiometric compound. The nonstoichiometric materials are important because they
provide the most straightforward path to explain the main features of our model and to highlight the role of the amphoteric defects which, as will be argued later, are solely responsible for the superconductivity in all high temperature cuprate superconductors.

Here we focus our considerations on a model cuprate superconductor that is based on the most extensively studied YBa$_2$CuO$_{6+\delta}$ compound which is a charge transfer insulator for stoichiometric composition YBa$_2$CuO$_6$ ($\delta = 0$). We consider a generic case of single system of amphoteric defects associated with 2-D CuO$_2$ planes in which free holes originate from ADs acceptors ignoring the role of 1-D CuO chains that are known to affect the charge balance by providing additional holes to the CuO$_2$ planes. The effects of the 1-D CuO chains will be discussed later in the section V on chemical doping.

**Figure 3** shows the dependencies of the concentration of free holes as well as the concentrations of the defects in the $D^+$ and $A^-$ configuration on the total concentration of amphoteric defects, $N_{AD}$. All the concentrations are measured as fractions of the total concentration of Cu-O bonds. In these units the concentrations of amphoteric defects associated with a deviation from stoichiometry for YBa$_2$CuO$_{6+\delta}$ is given by $N_{AD} = \delta / 6$. The corresponding free hole concentrations can be calculated considering that the free holes are localized in 2-D CuO$_2$ planes with a constant density of states given by

$$G_{2D} = \frac{4\pi m^*_h}{h^3} = 4.2 \times 10^{14} \left(\frac{m^*_h}{m_e}\right) \text{[eV}^{-1}\text{cm}^{-2}]$$  \hspace{1cm} (1)

where $m^*_h$ and $m_e$ are the hole effective mass in the CTB and the free electron mass, respectively. Adopting the plane unit cell dimensions for YBCO $a = 0.38$ nm and $b = 0.39$ nm yields the density of states as a fraction of the concentration of CuO bonds$^{42}$

$$G_{2Dfr} = 0.63 \left(\frac{m_h^*}{m_e}\right) \text{[eV}^{-1}] \text{.}$$  \hspace{1cm} (2)

Since the interplanar lattice constant $c = 1.17$ nm then the equivalent 3-dimensional density of states is given by

$$G_{3D} = \frac{G_{2D}}{c} = 3.5 \times 10^{21} \left(\frac{m_h^*}{m_e}\right) \text{[eV}^{-1}\text{cm}^{-3}] \text{.}$$  \hspace{1cm} (3)

As is illustrated in **Fig. 3** for the charge transition state located in the CTB an initial increase of the non-stoichiometry $N_{AD}$ produces amphoteric defects in the acceptor configuration that contribute free holes to the CTB i.e $\rho = N_{A^-}$. The free holes frustrate the antiferromagnetic order of
Cu magnetic moments leading to a decrease of the antiferromagnetic coupling and a reduction in the Neel temperature. Furthermore, the increase of the free hole concentration downward shifts the Fermi energy in the CTB until it reaches the charge transition state $E_{AD}(-/+)$.

Since this Fermi energy corresponds to the equal formation energy of the amphoteric defects in the acceptor and donor configuration an additional increase of $N_{AD}$ leads to formation of equal concentrations of $A^-$ and $D^+$ that compensate each other stabilizing the Fermi energy at $E_F = E_{FS} = E_{AD}(-/+)$ and the corresponding hole concentration at $p = p_s$. This is a critical transition point as a further increase of $N_{AD}$ increases the concentration of the defects in the $D^+$ configuration which, as will be shown later are responsible for the superconductivity. It is easy to see that the hole concentration, $p$ and the concentrations of ADs in the acceptor, $N_{A^-}$ and donor, $N_{D^+}$ configuration are given by:

\[ p = N_{AD} \quad \text{for} \quad N_{AD} \leq p_s \]  \hspace{1cm} (4a)
\[ p = p_s \quad \text{for} \quad N_{AD} > p_s \]

\[ N_{A^-} = N_{AD} \quad \text{for} \quad N_{AD} \leq p_s \]  \hspace{1cm} (4b)
\[ N_{A^-} = \frac{(N_{AD} + p_s)}{2} \quad \text{for} \quad N_{AD} > p_s \]

and

\[ N_{D^+} = 0 \quad \text{for} \quad N_{AD} \leq p_s \]  \hspace{1cm} (4c)
\[ N_{D^+} = \frac{(N_{AD} - p_s)}{2} \quad \text{for} \quad N_{AD} > p_s \]

The equilibrium condition between amphoteric defects in the acceptor, $A^-$ and donor, $D^+$ configurations for $p_s \leq N_{AD}$ is achieved at high temperature thru a capture of two charges. Capture of two holes that transforms $A^-$ into $D^+$ is described by the reactions,

\[ A^- + h \rightarrow A^0 \]  \hspace{1cm} (5a)
\[ A^0 \Rightarrow D^0 \]  \hspace{1cm} (5b)
\[ D^0 + h \rightarrow D^+ \]  \hspace{1cm} (5c)

with an analogous set of reactions for transformation of a $D^+$ into $A^-$ by sequential capture of two
electrons:

\[ D^+ + e \rightarrow D^0 \]  \hspace{1cm} (6a)

\[ D^0 \Rightarrow A^0 \]  \hspace{1cm} (6b)

\[ A^0 + e \rightarrow A^- \]  \hspace{1cm} (6c)

Although the capture of the first hole (electron) in the reaction 5(a) (6(a)) requires the excitation energy \( U = E_{AD}(-/+) - E_A(-/0) \) \( (U = E_D(0/+)-E_{AD}(-/+)) \) this energy is regained by adding another hole (electron) to the defect in the reaction 5(c) (6(c)). This is a very important property of the ADs as it drives the reaction, \( 2AD^0 \rightarrow D^+ + A^- \), in which two neutral ADs lower their energy by exchanging charges and producing \( D^+ \) defect with localized pair of equivalent holes and an \( A^- \) defect with localized pair of equivalent electrons bound by the energy \(-U\). These properties of ADs create a unique physical system of free holes whose Fermi energy is resonant with the energy level of hole pairs localized on the randomly distributed, isolated \( D^+ \) donor defects.

In general terms a similar system was previously envisioned as a possible scheme to explain superconductivity in cuprates where it was argued that the very small coherence length indicated that the superconductivity in these materials has to be mediated by a field, \( \Phi \) of highly localized bosons.\(^4\) Here we show that this condition is satisfied by an ensemble of randomly distributed \( D^+ \) defect centers localizing two holes with the binding energy \( U \) and acting as a boson field \( \Phi \) leading to the transition,

\[ 2h \rightarrow \Phi \rightarrow 2h, \]  \hspace{1cm} (7)

in which localized zero momentum boson field of \( D^+ \) defect centers forces two mobile holes with equal and opposite momenta to form Cooper pairs that at low enough temperature evolve into a coherent superconducting phase. It should be noted that because of the planar nature of the Cu-O bonds the localization of the \( D^+ \) defects is anisotropic with the spatial extent restricted to few nearest neighbors in the CuO\(_2\) plane and with even stricter confinement in the direction perpendicular to the CuO\(_2\) plane. This is fully consistent with a small coherence length of \( \xi \approx 2.5 \) nm in the CuO\(_2\) plane and an extraordinarily small \( \xi \approx 0.8 \) nm perpendicular to the plane found in cuprate superconductors.\(^4\) Also, as was argued in ref. \(^4\) the coupling between the fermion
and boson systems does not depend on the internal structure of the localized centers that form the boson field. This means it is not affected by the microscopic structure of the $D^+$ defects localizing hole pairs.

It is obvious from the above considerations that cuprates cannot be considered classical metals with simple metallic bonds and a free carrier gas described by the Fermi liquid theory. Instead, the electrical properties of cuprates are determined by interactions between free hole gas and the Cu-O bonding structure that is critically affected by the material stoichiometry. Thus, in this case the Cu and/or O dangling bonds play a role of so called “internal coordinates” which, as has been hypothesized before, could play a key role in determining normal and superconducting properties of unconventional superconductors.\([12]\)

An explicit theory of superconductivity in a system with localized negative-$U$ centers was previously developed to consider the experimentally observed enhancement of the critical temperature in superconducting eutectic Al-Si alloys.\([11,13]\) It was shown that interaction of the Al metal electrons with negative-$U$ centers of amorphous phase of Si leads to enhancement of the critical temperature of Al metal.\([13]\) The theory has also yielded an expression for the critical temperature of a free fermion gas interacting with localized negative-$U$ bosons. Adopting this approach to our presently considered system allows expressing the critical temperature for superconducting transition in terms of equations where key parameters can be derived from the AD model.

The critical temperature $T_c$ for superconducting transition is obtained solving the equations,\([13]\)

$$1 = |U_{\text{eff}}| \Gamma \left[ \varphi \left( T_c, E_r^2 \right) - \varphi \left( T_c, E_r^2 + |\nu_{\text{AD}}^2| N_{D^+} \right) \right]$$  \quad (8)

with

$$\varphi \left( T_c, E_r^2 \right) = \frac{1}{\pi (\Gamma^2 + E_r^2)} \left[ \ln \frac{2\gamma (\Gamma^2 + E_r^2)^{\frac{3}{2}}}{\pi T_c} - \frac{\Gamma}{T_c} \tan^{-1} \left( \frac{E_r}{\Gamma} \right) \right],$$  \quad (9)

$$U_{\text{eff}} = \frac{U}{1 + \left( \frac{U}{\pi E_r} \right) \tan^{-1} \left( \frac{E_r}{T_c} \right)} < 0,$$  \quad (10)

and $\Gamma = \pi |\nu_{\text{AD}}^2| G(0)$, where $N_{D^+}$ is the concentration of localized hole pairs equal to the concentration of the ADs in the donor configuration, $E_r = E_{AD}(+/−) - E_F$ is the energy of the charge transition state of ADs between donor and acceptor configuration relative to the Fermi energy, $U$ is the negative energy localizing two holes on the $D^+$ defects, $|\nu_{\text{AD}}^2|$ is the parameter describ-
ing the strength of the coupling between free holes and hole pairs localized on the $D^+$ defects, $G(0) = G_{2Df}$, is the density of states of free holes at the Fermi energy and $\gamma$ is Euler’s constant.

The dependencies of the free hole concentration ($p$) and the concentrations of ADs in the acceptor ($N_{A^-}$) and donor configuration ($N_{D^+}$) on the concentration of the ADs ($N_{AD}$) given by relations 4(a) to 4(c) are shown in Fig. 3 assuming $p_s = 0.05$. Using Eqs. (1) and (2) with the hole effective mass $m^*_h = 0.62m_e$ this $p_s$ corresponds to 2-D hole concentration of $3.4 \times 10^{13} \text{ cm}^{-2}$ and the Fermi energy located at 0.13 eV below the CTB edge. The solid black line represents critical superconducting temperature $T_c$ obtained by solving Eqs. (8) to (10). As expected, $T_c$ is increasing with the concentration of the localized hole pairs, $N_{D^+}$. All the calculations in this paper were performed with a single set of parameters, $U = -0.52 \text{ eV}$, $G(0) = 0.39 = 2.6 \times 10^{14} \text{ eV}^{-1} \text{ cm}^{-2}$, $|\nu_{AD}^2| = 0.16 \text{ eV}$ and $\Gamma = 0.2 \text{ eV}$. Considering the number of the parameters these is not a unique set. The parameter space was investigated and the final set of parameters was chosen to yield a reasonable overall agreement of the calculated quantities with typical experimental data.

The $T_c$ plotted in Fig. 3(h) was calculated for $E_r = 0$, i.e for the Fermi energy resonant with the charge transition state, $E_{AD}(+/−)$ between donor and acceptor configuration. To illustrate the resonant character of the superconducting coupling, the lowest panel (Fig. 3 (i-k)) shows the dependence of $T_c$ on the deviation $E_r/\Gamma$ of the Fermi energy from the resonance, calculated for three different concentrations of ADs. It is seen that a departure from the resonance condition leads to a rapid reduction of $T_c$. These results highlight the importance of the high temperature processing whose objective is not only to generate free holes but more importantly to create a thermodynamic equilibrium with maximized concentration of isolated boson $D^+$ centers and the Fermi energy as close to resonance with $E_{AD}(+/−)$ as possible. It also raises an interesting issue of the extent to which the resonant conditions obtained at high processing temperature are still preserved at low temperatures at which superconductivity is measured.

The calculations in Fig. 3 showing the dependence of $T_c$ on $N_{D^+}$ were carried out assuming an idealized system of randomly distributed, noninteracting defects that are in a stable thermodynamic equilibrium that has been achieved during high temperature processing. However, since maintaining the superconducting resonance coupling condition requires that $N_{A^-} = p_s + N_{D^+}$ this means that attaining a higher $T_c$ through an increase in $N_{D^+}$ has to be compensated by equal increase in the concentration of the negatively charged ADs in the acceptor configuration, $N_{A^-}$. This leads to a decrease of the average distance between $A^-$ and $D^+$ centers and an increased probability for a passivation by formation of a neutral $A^-D^+$ complexes that deactivate $D^+$ resulting in
FIG. 3. (a), (b) and (c) downward shift and stabilization of the Fermi energy in the CTB with increasing concentration of ADs with the formation energy shown in (d); schematic representation of the relationship between free holes and ADs in the acceptor and donor configuration (e), (f) and (g). Two holes localized on the donor defect force formation of a pair of free holes with opposite momenta (f) and (g). Dependence of the free hole concentration along with concentrations of the defects in the acceptor and donor configurations as functions of the total concentration of amphoteric defects (e). The black solid line shows the calculated critical temperature $T_c$. The bottom panel (i), (j) and (k) shows the dependence of the $T_c$ on the deviation from the resonance condition $E_F = E_{AD}(+/-)$ for three different concentrations $N_{AD}$.

To account for this effect, we adopt a simplified approach based on the concept of metal-insulator transition in doped semiconductors in which we assume that there is a critical concentration of ADs in the acceptor configuration, $N_{cr}^{A^-}$ at which all $D^+$ will be passivated resulting in an abrupt cut-off of the superconductivity. To evaluate the effects of the passivation on the macroscopic superconductivity we consider how spatial fluctuations of the defect concentration,
$N_{AD}$ affect $N_{D^+}$ and thus also the critical temperature. A spatially inhomogeneously broadened concentration of the $N_{D^+}$ is given by

$$
N_{D^+}^{\text{br}} = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} N_{D^+}' \exp\left[-\frac{\left(N_{D^+}' - N_{D^+}\right)^2}{2\sigma^2}\right] dN_{D^+}'
$$

(11)

where $\sigma$ is the broadening parameter,

$$
N_{D^+} = \frac{(N_{AD} - p_s)}{2} \quad \text{for } N_{AD} < 2N_{A^-}^{\text{cr}} - p_s
$$

and

$$
N_{D^+} = 0 \quad \text{for } N_{AD} \geq 2N_{A^-}^{\text{cr}} - p_s
$$

The spatially broadened concentration of the AD donors $N_{D^+}^{\text{br}}$ given by Eq. (11) can then be used to calculate the critical temperature. Figure 4 shows the dependence of superconducting transition temperatures $T_c$ on the $N_{AD}$ calculated using two different critical concentrations, $N_{A^-1}^{\text{cr}} = 2p_s = 0.1$ and $N_{A^-2}^{\text{cr}} = 2.2p_s = 0.11$ corresponding to $N_{AD1}^{\text{cr}} = 0.15$ and $N_{AD2}^{\text{cr}} = 0.17$. It is seen that incorporation of the broadening for the defect distribution leads to a gradual decrease of the $N_{D^+}$ and thus also $T_c$ at large $N_{AD}$. This results in a characteristic dome-like shape in the $N_{AD}$ dependence of $T_c$ with five doping regions. In the first region, $N_{AD} < 0.05$ ($\delta < 0.3$) the material has low hole concentration, $p = N_{AD}$ which is consistent with the high resistivity antiferromagnetic region experimentally observed in all high $T_c$ cuprates. For $N_{AD} \geq p_s$ the hole concentration stabilizes at $p_s$. The stabilization is accompanied by formation of the hole boson pair $D^+$ centers and the onset of the superconductivity. In this concentration range commonly termed as the underdoped region the $T_c$ is monotonically increasing with $N_{AD}$. At even higher $N_{AD}$ the $T_c$ begins to decrease when the hole boson pair $D^+$ centers become progressively passivated by $A^-$ defects. This range of concentration is referred to as an overdoped region. Finally, $T_c$ goes to zero when all $D^+$ centers are passivated and, as is shown in Fig. 4 (e) the defects form a narrow band of extended states at the charge transition state $E_{AD}(+/−)$ leading to an increased density of states at the Fermi energy and the onset of metallic conductivity. It is important to note that in this simple picture the optimum doping region just corresponds to the maximum $T_c$ in the transition from the underdoped region with increasing $D^+$ and $T_c$ to the overdoped region with the onset of the defect passivation, decreasing concentration of isolated $D^+$ and thus also $T_c$. Actually, the dependence of $N_{D^+}$ and $T_c$ on $N_{AD}$ in the optimum doping region is more complicated since, as is shown in the
FIG. 4. (bottom panel) Dependence of critical temperature $T_c$ on the concentration of ADs for two different cut-off densities $N_A^{cr} = 0.1$ (dark green) and 0.11 (light green). The plots of $N_A^-$ and $N_D^+$ represent the former case. Middle panel illustrates schematically the evolution of the material properties from high resistivity antiferromagnet with all ADs in the acceptor configuration (f) to underdoped superconductor with increasing concentration of the localized boson pairs (g), to optimally doped material with maximum density of boson pairs (h), to overdoped superconductor with a fraction of $D^+$ passivated by $A^-$ defects (i) finally to non-superconducting metallic conductor with all $D^+$ passivated by $A^-$ (j). The top panel shows the corresponding dependence of the Fermi energy in the CTB and associated change in the density of states of defects in different configurations.

Bottom panel of Fig. 3 $T_c$ is strongly affected by any deviation from $E_r = 0$ resonance that in turn depends on the sample preparation conditions. This will be further discussed in section VI of the paper.

Besides the good description of the dome like phase diagram the AD model accounts for some other well experimentally established but poorly understood features of superconducting cuprates. One of the mysterious characteristics of cuprates is the universal dependence of the critical temperature on the superconducting phase or superfluid density measured by muon-spin-relaxation\cite{45} where the same simple relationship between $T_c$ and superfluid density was found for different cuprates in the underdoped\cite{45} and to some extent in the overdoped\cite{45} region. This relationship can be easily understood considering that, as is shown Fig. 3, the superfluid density and the critical
temperature are proportional to $N_{D+}$ which is the only variable parameter in the Eqs. (8) to (10) to calculate $T_c$. All the other parameters are determined by properties of 2-D CuO$_2$ planes that are very similar for all cuprates leading to shown in Fig. 4 universal $T_c$ dependence on the doping for all cuprates in the underdoped region. It has been shown that the difference in the maximum $T_c$ in the optimally doped region can be attributed to the number of CuO$_2$ planes per material formula in different cuprates. Thus, it has been demonstrated that in HgBa$_2$Ca$_{m-1}$Cu$_m$O$_y$ the maximum $T_c$ is increasing from $T_c = 94$ K for $m = 1$ to 134 K for $m = 3$.[47] This again has a simple explanation as with increasing $m$ the same concentration of ADs corresponds to larger average distance between defects and thus also larger $N_{cr}^+$ which as is shown in Fig. 3 shifts the optimum doping to larger $N_{AD}$ and higher $T_c$. The decrease in $T_c$ for $m > 3$ could be associated with reduced hole confinement in the CuO$_2$ planes.

V. CHEMICAL DOPING

The superconductivity in cuprates was first discovered in intentionally chemically doped La$_{2-x}$Ba$_x$CuO$_4$[1] where Ba atoms partially substituting La atoms contribute free holes to the CTB. The large majority of subsequent work was done on p-type materials although in most instances the p-type conductivity was realized by varying the O content rather than chemical doping. The dominant role of nonstoichiometry was clearly demonstrated in the case of single crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ where[41] the properties of the crystals were varied across the entire superconducting dome by increasing O content, $x$. Also, it has turned out that more elaborate annealing conditions in O-rich environment can also produce superconductivity in La$_2$CuO$_4$, which is the parent compound for the extensively studied La$_{2-x}$Ba$_{1-x}$CuO$_4$ and La$_{2-x}$Sr$_{1-x}$CuO$_4$ chemically doped with Ba or Sr.[48] These findings indicated that the chemical p-type doping simplifies sample preparation conditions to achieve optimum critical temperature but is not required for superconductivity.

A critical advancement in the research on superconducting cuprates was an unanticipated discovery of superconductivity in materials chemically doped with donors.[49] It was found that, as expected, Ln$_{2-x}$Ce$_x$CuO$_4$ in which four valent Ce partially replaces trivalent lanthanide atoms (Ln=Pr, Nd) is a non-superconducting electron conductor. Surprisingly and somewhat accidentally it was found that the compounds become superconducting when subjected to high temperature annealing under O-deficient conditions.[49] Interestingly the properties of these n-type superconduct-
ing cuprates exhibit certain qualitative similarities with the p-type counterparts. Most prominently they show a dome like dependence of the critical temperature on the doping although, with much lower critical temperature and a narrower superconducting doping range.\textsuperscript{50,51} A striking difference between these two types of superconductors is that producing superconductivity in n-type cuprates always requires more elaborate and often extreme annealing procedures\textsuperscript{52} with very specific, well controlled O ambient whereas in p-type cuprates a higher $T_c$ superconductivity can be realized with much simpler sample preparation procedures. It should be emphasized however that in both instances optimization of superconducting properties involves sample processing aimed at varying the O content.\textsuperscript{53,54}

An important and mysterious feature of the n-type doped cuprates is that they do not consistently show an n-type normal state conductivity.\textsuperscript{55} In addition, there are experimental indications that holes rather than electrons are responsible for superconductivity in these materials.\textsuperscript{55–57} Comparing the main features of the two types of chemically doped superconducting cuprates it can be concluded that in contrast to p-type n-type cuprates are much more difficult to synthesize, have inferior superconducting properties and do not exhibit specific, well-defined type of normal state conductivity.

Considering the discussed in section II bipolar nature of the amphoteric defects in semiconductors it would be tempting and most straightforward to assume that, as is shown in Fig. 1 (a), chemical n-type doping stabilizes the Fermi level at the charge transition state located in the conduction band or UHB and the superconducting phase of free electrons is associated with formation of electron Cooper pairs coupled to electron pairs localized on $A^-$ centers. However, this would require a large, comparable to the band gap, downward shifts of UHB edge energy relative to the charge transition state energy, $E_{\text{AD}}(+/−)$. It is an unlikely scenario, as all these energies are defined by the nature of the highly localized Cu-O bonds in CuO$_2$ planes that are not significantly different for n- and p-type doped cuprates. Also, direct x-ray photoelectron spectroscopy measurements found only small differences in the locations of the Fermi energy in p-type compared with n-type superconducting cuprates.\textsuperscript{58} Therefore, there is a need to envision the case of a cuprate doped with chemical donors contributing electrons to the UHB but with the charge transition state still located in the CTB.

In order to evaluate how the chemical doping affects the superconductivity we consider a prototypical generic cuprate chemically doped with either acceptors or donors. Again, the properties of the material are determined by interactions between the intentionally introduced dopants and the
ADs whose concentration $N_{AD}$ depends on the material stoichiometry. As is shown in the upper panel of Fig. 5 chemical doping of a stoichiometric cuprate with $N_a$ acceptors ($N_d$ donors) produces p-type (n-type) conductor with $p = N_a$ holes ($n = N_d$ electrons) placing the Fermi energy in the CTB (UHB). In both cases increasing the nonstoichiometry and thus also $N_{AD}$ results in a downward shift of the Fermi energy towards $E_{AD}(+/−)$. Once this level is reached the charge balance between chemical dopants and ADs in the donor and acceptor configuration is given by:

\begin{align}
N_{A−} &= \frac{N_{AD} + (p_s - N_{a−})}{2} \tag{12a} \\
N_{A−} &= \frac{N_{AD} - (p_s - N_{a−})}{2} \tag{12b}
\end{align}

for doping with $N_a$ chemical acceptors, and

\begin{align}
N_{A−} &= \frac{N_{AD} + (p_s + N_{d+})}{2} \tag{13a} \\
N_{D+} &= \frac{N_{AD} - (p_s + N_{d+})}{2} \tag{13b}
\end{align}

for doping with $N_d$ of chemical donors. Here we assume that that the charge transition state for chemical acceptors (donors) lies well below (above) the CTB edge and all of the dopants are ionized.

The concentrations of ADs in the acceptor and donor configurations as functions of $N_{AD}$ given by Eqs. (12) and (13) are shown in Fig. 5 with the right-hand side representing p-type and the left-hand side n-type doping. The same chemical doping concentration, $N_a = N_d = 0.4p_s$ was assumed for both cases. It should be noted however that the main conclusions of the following considerations are not affected by the chemical doping levels. The chief effect of the chemical doping is to change the balance between concentration of ADs in the acceptor ($A−$) and donor ($D+)$ configuration with p-type (n-type) doping reducing (increasing) $N_{A−}$ and increasing (reducing) $N_{D+}$. This has a direct effect on the superconductivity because $T_c$ is proportional to $N_{D+}$ and as seen in the Fig. 5 p-type (n-type) chemical doping reduces (increases) the concentration of $N_{AD}$ (nonstoichiometry) required for the onset of the superconducting dome shifting it from $N_{AD} \approx 0.05$ for p-type to $N_{AD} \approx 0.09$ for n-type doping. Furthermore, since the p-type (n-type) chemical doping decreases (increases) the concentration of $N_{A−}$ it also has an effect on the termination of the $T_c$ dome at high $N_{AD}$ where, as has been shown in Fig. 4 the decrease of $T_c$ is associated
with passivation of $D^+$ by $A^-$ centers. **Figure 5** shows that adopting the same value $N_{A^-}^{cr} = 2p_i$ for both p-type and n-type doping terminates $T_c$ at $N_{AD} \approx 0.18$ for p-type and at $N_{AD} \approx 0.13$ for n-type doping. This distinct asymmetry in the maximum $T_c$ and the shape of the phase diagram for p-type and n-type doping is in a remarkable qualitative agreement with existing experimental data.\(^5^0\) The lowest panel in **Fig. 5** shows color-coded two dimensional maps of the dependence of $T_c$ on the $N_{AD}$ and the deviation of the Fermi energy from the resonance condition $E_r/\Gamma = [E_F - E_{AD}(+/−)]/\Gamma = 0$. It is seen that close to the optimum doping $T_c$ becomes less sensitive to the deviation of the Fermi energy from the resonance. Therefore, as will be discussed later, it is possible that with specific material processing conditions the optimum $T_c$ can be achieved under off resonance conditions ($E_r \neq 0$) but with higher $N_{D^+}$.

Chemical doping provides an insight into the origin of the double dome structure in YBa$_2$CuO$_6+\delta$ where two plateaus’ one with $T_C \approx 60$ K and the other $T_C \approx 90$ K are observed in the critical temperature dependence on the excess oxygen content, $\delta$.\(^4^7\)\(^5^9\) The unique characteristic of YBa$_2$CuO$_6+\delta$ is that in addition to the standard 2-dimensional CuO$_2$ planes Cu and O form also 1-dimensional CuO chains. Changing the O content produces dangling bond like defects in both chains and planes. However, the dangling bonds in the chains act only as external sources of holes to be transferred to the conducting CuO$_2$ planes. Therefore, the role of the chains is similar to the p-type chemical doping which shifts the saturation of the hole concentration and thus also the onset for the formation of $N_{D^+}$ to lower nonstoichiometry, $\delta$. The experiments indicate that the hole concentration originating from the chains reaches the 60 K plateaus for $0.7 \geq \delta \geq 0.6$ ($0.12 \geq N_{AD} \geq 0.1$). At larger $\delta$ the concentration of $D^+$ is controlled by holes originating from the planes leading to the higher $T_c$ of 90 K.\(^6^0\)

In the above considerations we have shown that the superconductivity in cuprates is associated with the presence of ADs whose concentration depends on the Cu/O ratio that can be controlled by proper material processing conditions. It is not overstatement to claim that sample preparation conditions are the most critical factor determining superconducting properties of all cuprate superconductors. This is strongly supported by the fact that the optimum superconducting properties are frequently achieved with materials processing procedures based on a trial-and-error approach. Also it was shown that annealing under O-rich or O-deficient conditions can reversibly change the same material between superconductor and normal conductor phase.\(^6^1\) Such behavior is fully consistent with our model as these processing conditions provide the most straightforward way to change the chemical potential of O and thus also the formation energy and concentration of
FIG. 5. Dependence of the critical temperature $T_c$ on the concentration of amphoteric defects ($N_{AD}$) for a cuprate chemically doped with $N_a$ acceptors (right side panel) or $N_d$ donors (left side panel) assuming the same doping level $N_a = N_d = 0.4p_s$. The calculated $T_c$ was broadened with the same $N_{cr}^{AD} = 2p_s$ for both doping conditions. The straight lines show the concentrations of free carriers as well as concentrations of the ADs in the donor ($D^+$) and acceptor ($A^-$) configuration. The low panel shows color-coded two-dimensional maps of $T_c$ vs NAD and the Fermi energy relative to the charge transition $E_r/\Gamma = E_F - [E_{AD}(-/+) / \Gamma]$. 

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ADs. Also, it explains why achieving superconductivity in chemically n-type doped cuprates always require so extreme processing conditions. It is because in this case compensation of the chemical donors needed to move the Fermi energy into the CTB requires more ADs in acceptor configuration that have detrimental effect on superconductivity.

Although changing material stoichiometry is the most straightforward way to control concentration of ADs it should be emphasized that at high temperatures even a stoichiometric material can have high thermodynamic equilibrium concentration of ADs in the form of O and Cu vacancies. The defects transform between donor and acceptor configuration and reach the minimum energy for the Fermi energy stabilized at the charge transition state, $E_{AD}(+/−)$. The high temperature defect configuration can be frozen with a rapid cooling that is frequently used in preparation of superconducting cuprates. This means that, in general, the electrical properties of cuprates are not determined by chemical doping and/or excess or deficiency of oxygen and that with proper high temperature processing superconductivity could be achieved in undoped stoichiometric cuprates. Indeed, extensive annealing studies aimed at control of the O content have shown that La$_2$CuO$_4$ which is a parent compound for a number of p-type doped superconductors$^{48}$ and Pr$_2$CuO$_4$ a parent compound n-type superconductor$^{54}$ exhibit superconducting properties without or with insignificantly small chemical doping.

All the above considerations lead to very important conclusions regarding superconducting properties of cuprates. They demonstrate that amphoteric defects are exclusively responsible for the superconductivity of mobile holes interacting with hole pairs localized on amphoteric defects in the donor configuration, $D^+$. The p-type or n-type chemical doping is neither necessary nor sufficient condition for superconductivity. The role of chemical doping is limited to changing the balance between ADs in the donor and acceptor configuration with p-type (n-type) doping increasing (decreasing) the concentration of localized $D^+$ centers resulting in enhancement (reduction) of superconducting properties.

VI. EFFECTS OF EXTERNAL PERTURBATIONS

The present calculations of the superconducting properties tacitly assume that the hole concentration as well as concentrations of ADs in the donor and acceptor configurations are determined by the low temperature thermodynamic equilibrium with the Fermi energy in resonance with $E_{AD}(−/+).$ In general, the assumption cannot be justified as preparation of superconducting
cuprates requires high temperature processing followed by specific cooling conditions indicating that the low temperature superconducting properties are determined by the O content and a balance between ADs in donor and acceptor configuration frozen at some higher temperature. The temperature has to be high enough to allow for the transformation of ADs between donor and acceptor configuration but also low enough to assure that the frozen configuration is as close as possible to the optimum conditions for the superconductivity. The complexity of the sample processing procedures to achieve the optimum superconducting properties of cuprates can be attributed to three energy scales relevant to this problem. First, shown in Fig. 2(c) energy barrier $E_b$ which affects the balance between ADs in the donor and acceptor configuration second, the negative-$U$ energy and third the formation energy of the ADs, $E_{fA}(E_F) = E_{fD}(E_F)$ whose value for $E_F = E_{AD}(-/+)$ determines their total concentration. The latter energy depends on the non-stoichiometry given by Cu to O ratio. Additional factor adding to the complexity of the system is that, as is shown in Fig. 5 the concentration of the ADs in the donor and acceptor configuration can be affected by the chemical doping.

As has been shown in sections III and IV the highest $T_c$ is obtained for the Fermi energy at the resonance with $E_{AD}(-/+)$ ($E_r = 0$) and with maximized concentration of isolated $D^+$ centers. Unfortunately, considering the complex nature of the cuprate materials it is not likely there could be a material processing path leading to achieving these two goals simultaneously. Consequently, all the materials processing procedures aimed at maximizing superconducting properties are compromises between attempts to reach the resonance conditions while maximizing concentration of isolated $D^+$ defects. To gain an insight into this intricate process we simplify this problem by considering two limiting cases. In the first case we assume a constant concentration of $D^+$ for both p-type and n-type cuprates. Then, as is shown in Fig. 6 (a) initially the Fermi energy is located below (above) $E_{AD}(-/+)$ for p-type (n-type) material. An optimization process reduces (increases) $N_A$- shifting the Fermi energy towards $E_{AD}(-/+)$ in both cases. In the optimized material $E_r \cong 0$ and $T_c$ reaches the maximum value. In the second limiting case the optimization process aims at maximizing $N_{D^+}$ even if it is done at the expense of missing the resonance conditions. As is shown in Fig. 6 (e) this leads to an optimum $T_c = T_{C, op}$ at $E_r = E_{r, op} \neq 0$. It is obvious that those two limiting cases are gross simplifications of much more complex processes. However, they provide intuitive insights for understanding of the mechanism of the optimal doping as well as effects of external perturbation on the superconducting properties of cuprates.

Results in Figure 4 show that the first of the discussed above limiting cases applies to the dop-
ing region where the ADs are well isolated and do not interact with each other and the maximized $T_c$ is solely determined by the concentration of $N_{D^+}$ corresponding to the resonance condition ($E_r \approx 0$). This leads to the experimentally observed universal dependence of $T_c$ on the superfluid density in the underdoped region.\cite{45} However, increasing the concentration of ADs can change the optimum processing conditions towards the second limiting case where an increase in $T_c$ associated with increase of the superfluid density $N_{D^+}$ is compensated by reduction of $T_c$ caused by shift of the Fermi energy to off resonance conditions ($E_r \neq 0$). This results in a saturation or even a decrease of $T_c$ despite an increase of the superfluid density $N_{D^+}$.\cite{45,46} Such material specific saturation of the optimum $T_c$ is clearly observed in superconducting cuprates.\cite{45} As has been discussed in section III at even higher concentration of ADs corresponding to the overdoped region the superfluid density is reduced as $D^+$ are passivated by $A^-$. Again, $T_c$ becomes proportional to $N_{D^+}$ until it is terminated when all $D^+$ are passivated. This explains experimentally observed linear relationship between $T_c$ and superfluid density found in the overdoped region.\cite{45}

An interesting and perplexing feature of superconducting cuprates is their unusually complex dependence of $T_c$ on hydrostatic pressure.\cite{62,63} A large number of studies have shown that pressure dependencies of the critical temperature can vary widely, with $T_c$ pressure coefficients ranging from large positive to large negative values. More systematic studies have identified some important trends. Thus, it was found that application of hydrostatic pressure increases (decreases) $T_c$ in p-type (n-type) doped cuprates with the pressure induced $T_c$ change larger for non-optimally doped than for optimally doped materials.\cite{62} Furthermore, it was found that in some p-type cuprates optimized for the maximum $T_c$ application of very higher pressures results in a nonmonotonic dependence with an initial rapid increase followed by saturation or even decrease of $T_c$ at the highest pressures.\cite{21} Here we will show that the main characteristic features of these distinct pressure effects on $T_c$ can be understood in terms of the discussed above thermodynamic properties of ADs.

In order to evaluate the pressure effects on $T_c$ one needs to know how the pressure affects the charge transfer band (CTB) edge energy. Previous studies on charge transfer oxides have shown that application of hydrostatic pressure increases the width of the CTB and reduces the charge transfer gap.\cite{64} Adopting these findings and considering that the charge transition state $E_{AD}(-/+)$ of highly localized ADs is independent of pressure,\cite{65} indicates that application of hydrostatic pressure will result in an upward shift of the CTB edge and thus also the Fermi energy relative to $E_{AD}(-/+)$ directly affecting the resonance conditions for the maximum $T_c$. This leads to a distinct asymmetry in the effects of pressure on the $T_c$ in p-type and n-type superconducting
cuprates. Specifically, as is shown in the left side top panel of Fig. 6 the pressure induced upward shift of the CBT edge moves the Fermi energy towards (away) from the resonance resulting in an increase (decrease) of $T_c$ for p-type (n-type) cuprates. The initial relative pressure coefficient of $T_c$ ($d \ln T_c/dP$) is determined by shown in Fig. 6 bell-like shape of the dependence of $T_c$ on the deviation from the resonance condition, $E_r = 0$. Figure 6 (h) shows that the calculated pressure coefficient changes from large positive values for non-optimal p-type doping goes to zero for optimal doping and becomes negative for non-optimal n-type doping. This is in a good qualitative agreement with experimentally observed trends. Here $T_c$ was calculated with $N_{D^+} = 0.04$ and the other parameters the same as those used for the results shown in Figs. 3 and 4. The only additional parameter is the pressure induced shift of the Fermi energy relative to the charge transition state i.e. $dE_r/dP = d(E_F - E_{AD}(-/+)/dP$ which is equal to the pressure induced upward shift of the CTB edge energy. Here we find that an overall good explanation of the experimentally observed trends is obtained for $d(E_r/\Gamma)/dP = 0.01$ GPa or $dE_r/dP = 2$ meV/GPa which is in the range of typical values of pressure induced shifts of the valence band edges in semiconductors.

Figures 6 (d), (e) and (f) illustrate the effects of hydrostatic pressure on $T_c$ for the second discussed above limiting case where the optimum $T_c = T_{c,op}$ is achieved with maximized $N_{D^+}$. In order to model the pressure effects in HbBa$_2$Ca$_{m-1}$O$_{m+2}$ with $m = 1, 2, 3$ it is assumed that the optimized $N_{D^+}$ is increasing with $m$. Specifically, the calculations shown in Fig. 6 (i) and (j) were carried out for three different concentrations $N_{D^+} = 0.035, 0.04$ and 0.045 with the assumption that in all instances the optimal $T_c$ is reached for $E_r/\Gamma = -0.3$. Again, the other parameters have the same values as used in the previous calculations. It is seen that the pressure induced upward shift of the CTB edge moves the Fermi energy towards the resonance with $E_{AD}(-/+)/$ resulting in an increase of $T_c$. The $T_c$ reaches the maximum $T_{cR}$ for $E_r = 0$ and then decreases as $E_r$ becomes larger than 0. These calculations are in a very good qualitative agreement with experiments. They show that the optimized $T_c$ at the ambient pressure and the maximum $T_c$ at about 30 GPa exhibit a strong dependence on $N_{D^+}$ and thus also on the number of CuO$_2$ planes, $m$ in the unit cell. In contrast the pressure induced changes of $T_c(P) - T_c(P = 0)$ show very similar almost universal dependencies for all values of $N_{D^+}$. This result is a simple reflection of the fact that the $N_{D^+}$ has a negligible effect the bell-shaped dependence of $T_c$ on $N_{D^+}$.

Another characteristic and unusual feature of superconducting cuprates is a strong dependence of the critical temperature on the external bias where it was shown that application of high electric field can vary properties of thin cuprate films between superconducting and insulating
FIG. 6. (Left panel, a, b, c, g, h) Dependence of $T_c$ on hydrostatic pressure for p-type and n-type cuprates. In the p-type application of hydrostatic pressure to non-optimally doped cuprate ($E_r < 0$) shifts CTB and the Fermi energy towards resonance resulting in positive pressure coefficient. In non-optimally doped n-type cuprate ($E_r > 0$) application of pressure shifts the Fermi energy away from the resonance resulting in a negative pressure coefficient. The pressure coefficient for optimal doping ($E_r = 0$) equals 0 at low pressures.

(Right panel, d, e, f, i, j) Pressure dependence of $T_c$ optimized with maximum $N_{D^+}$ and $E_r < 0$. The upward shift of CTB and the Fermi energy increases $T_c$ until it reaches a maximum value $E_r = 0$. Further increase of the pressure leads to a decrease in $T_c$ as the Fermi energy shifts to off resonance conditions $E_r > 0$.

state. This is easy to understand in our model as the applied field affects the hole concentration and shifts the Fermi energy relative to the charge transition state $E_{AD}(-/+)$ affecting the resonance condition and thus also critical temperature. It is important to note that such external bias induced transition can be observed only for material with $N_{D^+} > 0$, that is, $N_{AD} > p_s$.

VII. SUMMARY AND OUTLOOK

In this paper we have presented a model of superconductivity mediated by amphoteric, negative-$U$ defects. The model is based on the vacancy-like defects in CuO$_2$ planes that can undergo a transformation between acceptor and donor configuration stabilizing Fermi energy and the hole concentration in the charge transition band. The amphoteric defects in the donor configuration trap two holes and act as highly localized preformed hole pairs facilitating the superconducting transition of the free hole gas. The critical temperature is fully determined by the
concentration of isolated amphoteric defects in the donor configuration and deviation of the Fermi energy from the energy of the charge transition state between acceptor and donor configuration. The model provides a unified explanation for key properties of the superconducting cuprates listed in points 1) to 5) in the introduction.

1) It is shown that the superconductivity in cuprates is innately related to presence of amphoteric defects in CuO$_2$ planes. Elaborate sample processing conditions with controlled Cu/O content ratio are required to maximize the concentration of preformed hole pairs $N_{D^+}$ while maintain the charge balance stabilizing the Fermi energy close to the resonance with the ADs charge transition state. (See Figs. 3, 5 and 6)

2) The dome-like dependence of the critical temperature is explained by doping induced increase of the concentration of performed hole pairs in the underdoped region. The reduction and the termination of $T_c$ at high doping levels is associated with passivation of the amphoteric defects in the donor and acceptor configuration (see Fig. 4). More subtle effects come into play close to the optimum doping where the critical temperature is affected by both the superfluid density and the deviation from resonance conditions. (See Figs. 3 and 6)

3) The universal dependence of the $T_c$ on the superconducting phase is the reflection of the fact that for the resonant coupling between free holes and preformed hole pairs the critical temperature is uniquely and in the same way affected by the superfluid density given by the concentration of the amphoteric defects in the donor configuration in all cuprates. (See Fig. 4)

4) It is shown that chemical doping with acceptors or donors is neither sufficient nor necessary condition for superconductivity which in both cases is associated with coupling of free holes in the charge transfer band to hole pairs localized on amphoteric defect donors. The asymmetry in the $T_c$ dependence on the doping originates from higher (lower) concentration of the defect donors in p-type (n-type) doped cuprates. (See Fig. 5)

5) The complex trends in the hydrostatic pressure dependence of the critical temperature are explained by the change in the resonance conditions resulting from the upward pressure induced shift of the charge transfer band and thus also the Fermi relative to the charge transition state of the ADs. (See Fig. 6)
This paper is focused on the effects of ADs on the superconducting properties of cuprates. However, it is obvious that the amphoteric defects play also critical role in determining normal state properties of these materials. In particular the electrical properties of the normal state are determined by the transport of free holes in the charge transfer band scattered by charged ADs in the donor and acceptor configuration. Furthermore, at higher temperatures electric charges can be transported within a defect band formed at the charge transition state $E_{AD}(-/+)$. The complex conductivity mechanism appears to be consistent with the observation that superconducting cuprates do not exhibit typical metallic, Fermi liquid like normal state properties. Another important issue is the extent to which the properties of normal state cuprates are affected by large concentration of the ADs in the acceptor configuration that is needed to stabilize the Fermi energy. Of particular significance could be the effect of resonance scattering of hole pairs on free of holes $A^-$ centers. This scattering is expected to affect the density of states in the charge transfer band and could be responsible for the normal state pseudogap effect that is routinely observed in superconducting cuprates. These and other issues relating to the normal state of superconducting cuprates will be addressed in future work.

The present paper is entirely devoted to the high $T_c$ cuprates that are by far the most prominent and representative group of unconventional superconductors in which there is convincing evidence that the superconductivity is not mediated by the electron phonon interaction. However, the class of unconventional superconductors is quite broad and includes a large variety of materials with varying degree of chemical complexity. Interestingly properties of some of these superconductors show a similarity to the properties of cuprates. Thus, the broad class of iron based superconductors (IBSC) with critical temperature of more than 50 K and semiconducting SrTiO$_3$ perovskite with $T_c$ of less than 1 K show a well-developed dome-like dependence of the critical temperature on various forms of doping. Again, it was shown that in both materials systems the superconductivity can be produced by varying only the crystal nonstoichiometry without any intentional chemical doping. Furthermore a large electron accumulation on the free surface of SrTiO$_3$ and at the superconducting interface between SrTiO$_3$/LaAlO$_3$ provide a strong evidence for an existence of localized defect charge transition state in the conduction band of SrTiO$_3$. All these observations strongly suggest that it could be interesting to look at the possibility that negative-$U$ amphoteric defects are also responsible for superconductivity in these and other similar materials.
AUTHOR CONTRIBUTIONS

Conceptualization: WW
Formal analysis: SW, WW
Funding acquisition: JWA, WW
Methodology: SW, WW
Software: SW
Supervision: WW
Validation and Visualization: SW
Writing - original draft: SW, WW
Writing - review and editing: SW, JWA, WW

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available upon reasonable request from the corresponding authors.

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