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ORIGINAL PAPER

Conductivity Properties of Perovskite Nickelates and Cuprates Depend on the Oxidation States of the Metal Ions

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Abstract

Superconducting nickelates in thin film perovskite structures, designed to be isostructural with the Cu(II) cuprates, have been discovered recently by Zhou et al. (Appl. Mater. Interfaces 10, 1463-1467, 1) and Li et al. (Nature 572, 624-627, 2) The strategies of both groups, to make nickelates as similar to the cuprates as possible by using planar NiO_2 superlattice structures, proved successful. Ni(I) and Ni(III) are superconducting in superlattices, although T_C is lower than in most Cu(II) cuprates. Here we find that a "3-oxidation states rule" applies to nickelate superlattices based on Ni(I) and Ni(III). It is predicted that the oxides of Ni(II), Cu(I), and Cu(III) cannot superconduct, because of violation of the 3-rule. This rule is derived here, along with other rules where the number of interacting oxidation states is decisive for the conduction properties of the metal ion. The Mott model is replaced by a free energy model.

Keywords Nickelate superconductivity · Superlattices · Oxidation state · Collapse of U · Pairing · Resistivity · Activation energy · MARCUS model · Magnetism

1 Introduction—Superconductivity (SC) in Nickel Perovskite Oxides

Transition metal oxides (TMO) possess a great variety of conduction properties. Recently two research teams have managed to make thin films of nickel oxides with valence Ni(III) [1] and Ni(I) [2, 3] superconducting (SC) in perovskite structures. The doped cuprate $La_{2-x}Sr_xCuO_4$ is SC for $0.06 < x < 0.25$ [4, 5]. $La_{2-x}Sr_xNiO_4$ with similar structure is non-metallic for $x < 0.8$, but approaches a metallic, non-SC state for $x > 0.8$ [6, 7]. NiO and La_2NiO_4 do not become SC. Ni(II) ions prefer local O_h symmetry [6] in the bulk. The 3d-e_g orbitals are degenerate and occupied with parallel spins according to Hund's rule. High spin makes superconductivity (SC) impossible.

In refs. [1–3], superlattices with NiO_2 planes are formed that emulate the CuO_2 planes in perovskite structures. The local Ni site symmetry is D_{4h}. The e_g degeneracy is broken, resulting in singlet spin for Ni(II). Ni(I) and Ni(III) are now SC, but Ni(II) remains non-SC. Cuprates are SC for Cu(II) but not for Cu(I) and Cu(III). These predictions for perovskites and the problem of "collapse of U" [8] will be explained below.

2 Conductivity in the Normal Region is due to Marcus Electron Transfer

Hubbard U is defined for Ni(II) by the charge transfer reaction [9]:

$$Ni_A(II) + Ni_B(II) + \hbar\omega \rightarrow Ni_A + Ni_B(III) \qquad (\hbar\omega = U) \tag{1}$$

The left member of Eq. (1) corresponds to the case of equal charge and alternant spin (AS) and the right member to alternant charge (AC). Hubbard $U \approx 4$ eV for Ni(II) and ≈2 eV for Cu(II). The Mott model works for "Mott insulators" but for doped TMOs the relative contribution to conductivity due to Eq. (1) is in fact negligible compared to the Marcus contribution.

Heikes and Johnston showed that conductivity in NiO increases by orders of magnitude in $Li_xNi_{1-x}O$ even at low doping [10]. Doping oxidizes a fraction (x) of Ni(II) to Ni(III). Electron transfer (ET) into the doped holes requires much less energy than with the Mott mechanism (U). Furthermore, in the Marcus model [11–17], a new hole is

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created on the site the electron was donated from. Sequential transfer along a chain of metal atoms is now possible.

Resistivity can be derived from ET probability in a hopping model [17]. By consecutive ET Ni(III) hole sites move in the direction of the field and act as electron acceptors according to:

$$\mathrm{Ni_A(III) + Ni_B(II) \rightarrow Ni_A(II) + Ni_B(III)} \quad \left(\Delta G^0 = 0\right) \tag{2}$$

The activation energy for Eq. (2), E_a, is due to small changes in geometry when center A accepts an electron donated by B [11].

The necessary reorganization energy is λ but the activation energy E_a in the case of the Marcus model is:

$$\mathrm{E}_a = \lambda/4(1-\Delta/\lambda)^2 < \lambda/4 \tag{3}$$

which tends to zero when the coupling Δ ($=2H_{12}$) tends to λ.

From the probability for electron transfer in a hopping model, we obtain a resistivity in good agreement with the experiments [17–19]. The Marcus model explains the far IR absorption. It also tells us that the resistance in TMO is due to bond length fluctuations depending on the number of electrons at a site. Bond length differences disappear in the metallic state, implying $\lambda = 0$. Collapse of λ and U is an experimental fact [7, 8, 20]. Keeping U constant in the Mott model for increased doping is unphysical.

The bond lengths increase when antibonding orbitals are filled. The reorganization energy λ may be calculated if the force constants are known [12–14]. The radius of the copper ions decreases in the series Cu(I) → Cu(III). In slightly doped perovskite Cu(II) cuprates, Cu(III) sites appear as local sites with shorter CuO bond lengths compared to the bulk. For increased dopings, there is increased delocalization ($\Delta/\lambda \rightarrow 0$). The point of full delocalization is not reached in cuprates since the normal region resistivity curves suddenly tend to zero between $x = 0.05$ and $x = 0.06$. Pairing and SC sets in [8, 21] and completes the delocalization and $\lambda = 0$.

E_A is on a free energy surface and can be thought of as the energy of a state. The activation energy U in the Mott model is incorrectly set equal to a constant in most papers. This is deeply unphysical since U and λ as defined above decrease by delocalization caused by doping. The activation energy for conductivity in the Mott model (U) is too large by at least a factor of four (Fig. 1) and decreases by further doping. The only reasonable interpretation of the far IR absorption tending to the Drude peak is that $E_a \rightarrow 0$ [18, 19, 22] (Fig. 2). At strong coupling, $\Delta = \lambda$ is clearly possible in TMO and leads to "collapse of U" [Eq. (3)].

Three other experimental facts are important: (1) repetitive systems are not always metals, (2) a system may be conducting even if it is not repetitive, (3) Marcus $E_a = 0$ is necessary and sufficient for metallic properties.

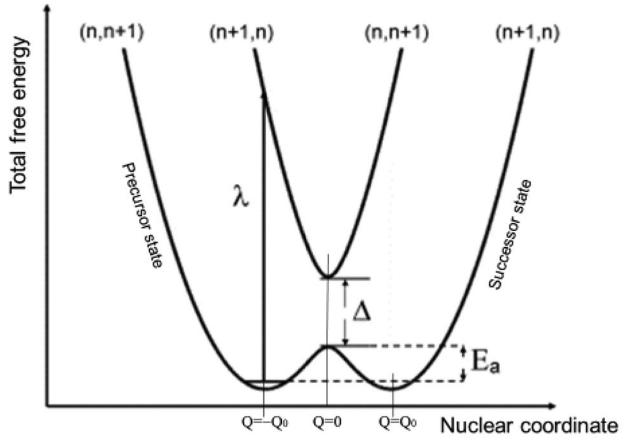

Fig. 1 The Marcus model [11–17]. The activation energy $E_a < \lambda/4$. $\Delta = 2H_{12}$ where H_{12} is the coupling

The BCS theory for SC in metals, based on **k**-space theories and Cooper pairs [23], was formulated in 1957. In those days, all known SCs were obtained by cooling ordinary metals below T_C. Thirty years later Bednorz and Müller found SC in a system derived directly from a local system [4]. Unfortunately the BCS model cannot be derived in a local model.

In 1937, de Boer and Verwey had found that the simple repetitive system NiO is an insulator in spite of an unfilled valence band [24]. Since then the Mott–Hubbard model has been considered necessary to "prevent" metallic conductivity in NiO. The insulating properties are in reality due to the fact that there is no place for the electron to jump in the undoped, local system. For low doping, we have to accept the fact that **r**-space theories have to be used, not **k**-space band models. The resistivity of

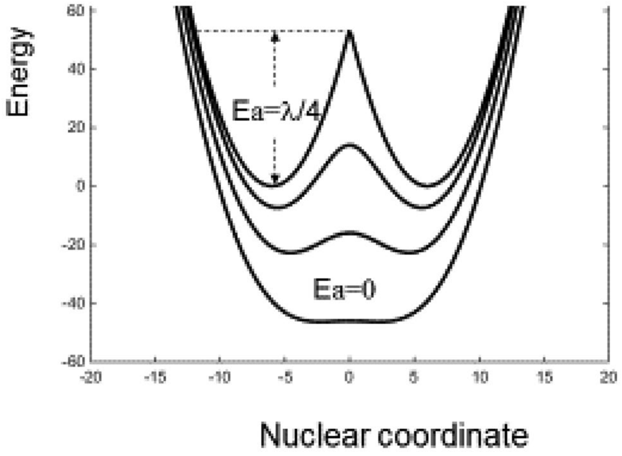

Fig. 2 Delocalization in the Marcus model from non-adiabatic coupling (top curve) to large coupling with $E_a = 0$ [18, 19]

$La_{2-x}Sr_xCuO_4$ in the normal region agrees with experimental results [12, 13, 17, 25].

During doping in the strong coupling case, $E_a \rightarrow 0$ and $\lambda \rightarrow 0$, meaning that TMO after enough doping may become metals without bond length dependence on site occupations, i.e., $\lambda = 0$.

3 Optical Spectra of Nickelates and Cuprates

The larger x in $La_{2-x}Sr_xCuO_4$ the larger the mixing entropy ΔS and the more lowering of the free energy (ΔG) of the mixed-valence system:

$$\Delta G = \Delta H - T\Delta S \quad (T\text{constant}) \tag{4}$$

From Eq. (4) follows that we may approach $\Delta G = \lambda = 0$ by doping (collapse of U). The peak at 2 eV in La_2CuO_4 must be $= U$ since there are no Cu(III) sites available at $x = 0$ (Eq. (1)). The larger the doping the larger the delocalization, and the smaller both λ and charge transfer energy U at a fixed structure. The collapse of U is approaching.

This way of reasoning does not include any "on-site repulsion." In fact the latter concept is strange since there are always compensating attractions which are not accounted for. In a Mott model, there is no explanation of the collapse of U. U is simply assumed to remain constant during doping, which is preposterous.

Collapse of U was first described without name in the important paper by Uchida et al. [8]. Reflectivity spectra of doped cuprates are analyzed particularly with respect to optical conductivity. There is spectral density transfer from ≈2 eV to the mid- and far IR region [7, 8, 26, 27]. In the Marcus model (Eq. (3)), E_a is much smaller than λ. The density of states in the far IR region builds up with doping. The Marcus model thus explains not only the far IR states but also their convergence into the Drude state.

In the nickelate $La_{2-x}Sr_xNiO_4$, there are two mid-infrared peaks at $x = 0.5$ and 1.5 eV [7, 28]. The peaks merge to a single peak at $x = 0.7$ tending to a Drude peak at $x = 0.9$. For $x > 1$, there is mixing between Ni(III) and Ni(IV) which leads to a quite wide Drude peak, with disappearing temperature dependence [7]. The resistivity as a function of temperature has a typical Marcus behavior from $x = 0.5$ to $x = 1.0$ with doping dependence (Fig. 1 of ref. [7]) and a minimum tending to zero with doping. For $x > 0.9$, there is increasing metallic behavior with $\lambda \rightarrow 0$. At $x = 1.2$, the bond distance difference is wiped out and we have a metal with only T or $T^{3/2}$ metallic temperature dependence in the resistivity [7].

Although $LaNiO_3$ is antiferromagnetic at very low temperatures [28–30], there is metallic conductivity of the form:

$$\rho(T) = A + BT^{3/2} \tag{5}$$

The 3/2 power of Eq. (5) and also a linear form originate in the Marcus equation, Eq. (2) [21, 22]. Most other $RNiO_3$ crystals ($R \neq La$) collapse to an insulating phase at low temperature with low symmetry. Above the transition temperature, the latter $RNiO_3$ systems, for instance $PrNiO_3$, have resistivities linear in T and are perfect metals [29, 30].

$LaNiO_3$ has metallic absorption of light up to 7 eV [28]. In a metal, the reorganization energy is = 0 since all electrons are equally distributed band electrons. There is no localization due to electronic motion and thus $\lambda = 0$. No doping is necessary for metallic behavior in the bulk phase of $LaNiO_3$ [1]. Ni(I) compounds are also SC in superlattices but doping is necessary in $NdNiO_2$ [18, 19].

One role of superlattices of nickelates is to break the degeneracy between the $3d$-e_g orbitals $x^2 - y^2$ and z^2 for Ni(II) to avoid the action of Hund's high-spin rule. It seems that Ni(II) has a role to play even in Ni(III) and Ni(I) systems. This will be explained in the next section. In "Sect. 5," we will show that the interactions for pair formation in Cu(II) compounds are absent for Ni(II) or Cu(III) with $3d^8$ occupation.

4 Pair Formation Consists of Two Coherent Marcus Steps

Very few TMO are metals in undoped form. It is therefore close to impossible to use **k**-space theory [23] of the BCS model to explain SC. Charge transfer excitations within the valence shell are hardly of any interest in BCS since U is always = 0. In Eq. (1) for cuprates La_2CuO_4, the excitation energy $\hbar\omega \approx 2$ eV, only half of its value for La_2NiO_4. The on-site repulsion for the larger ion [Ni(II)] should be smaller than for a smaller ion copper Cu(II)!

Exchange of electrons and electron pairs between two metal ions requires that the oxidation states on adjacent sites are strongly coupled since the distance between the metal ions is large. $Cu_A(II)/Cu_B(II)$ couples oxidation states $Cu_A(I)$ $Cu_B(III)$, resulting in electron pair transfer A → B [18]. In Ni(II), coupling is not possible in the same way; it is in fact forbidden.

A coherent transfer can be calculated by configuration interaction (CI). The overall symmetry is decisive for the overlap and similar to the case of the hydrogen molecule [31]. In the latter case, the so-called ionic wave functions play an unimportant role. Here we are talking about interaction between the alternant charge (AC) phase and the alternant spin (AS) phases. The AC phase corresponds to the ionic wave functions and the AS phase to the valence-bond wave function. The singlet spin function is written as $(\alpha\beta - \beta\alpha)$. α and β are orbital spins; a and b are wave functions centered on atoms A and B, respectively. From the AC "ionic" states, two functions arise:

$$\psi_2(1,2) = [a(1)a(2) + b(1)b(2)](\alpha\beta - \beta\alpha) \tag{6}$$

$$\psi_3(1,2) = [a(1)a(2) - b(1)b(2)](\alpha\beta - \beta\alpha) \tag{7}$$

The AS phase is represented by the valence bond wave function:

$$\psi_1(1,2) = [a(1)b(2) + b(1)a(2)](\alpha\beta - \beta\alpha) \tag{8}$$

The interaction between Ψ_1 and Ψ_2 provides the "glue" for pairing.

The electronic picture is shown in Fig. 3a, b in terms of oxidation states. Electron pairs are formed and move forward. The first ET step in Fig. 3a is ET from the Cu(I) to Cu(III), forming the intermediate Cu(II)/Cu(II) state. The second step is ET from the left Cu(II) to the right Cu(II) forming Cu(III)Cu(I). Coherent transfer is equivalent to CI between Ψ_1 and Ψ_2.

The a and b orbitals have e_g symmetry $[3d(x^2 - y^2)]$ on the sites A and B. The energy of the non-interacting Bogoliubov state Ψ_3 separates the SC gap from the pseudogap. The overlap integral:

$$\begin{aligned}&\int \Psi_1(1,2)\ \Psi_2(1,2)\ d\mathbf{r}_1 d\mathbf{r}_2\\ &= \int [a(1)b(2) + b(1)a(2)]\ [a(1)a(2) + b(1)b(2)]\ d\mathbf{r}_1 d\mathbf{r}_2\\ &= 4\int ab d\mathbf{r}_1\end{aligned} \tag{9}$$

The ground state of an electron pair contains components of all three oxidation states of copper: Cu(I), Cu(II), Cu(III) (with their coupled O2p components) in the description of the pair and its motion from A to B. Pair motion consists of two coherent ET steps. For $T > T_C$, thermal motion prevents coherence.

Here we have ignored the orbital of the oxygen atom in between the metal atoms. $a + b$ interacts with O2s and $a - b$ with O2p. At the end, we will be interested in the most antibonding combinations within this set, meaning that the antibonding orbitals with respect to O2p particularly. For the Cu(II) and Ni(II) perovskite structures, this means that some of the so-called 3 *deg* orbitals will be the highest occupied ones. The pattern of interactions in Eqs. (6)–(8) will not be disturbed.

In spite of large inter-metal distances between the metal ions, the coupling is large between the AC configurations and the cuprate (II)/(II) configuration in Eq. (9). Hence, pair formation and pair transfer need three stable oxidation states to describe pair transfer. CI between Ψ_1 and Ψ_2 leads to the electron pair ground state, followed in energy by the Bogoliubov state and the antibonding CI state. This is consistent with experiments which show that the SC gap and the pseudogap have a common origin.

If the increase of doping leads to a metal, the system becomes visibly delocalized in the sense that all bond length differences disappear [32]. Next we will study the coupling and find that transfer of two electrons has to take place through the same orbitals to obtain coherent pair transfer and SC.

5 Why SC in Cu(II), Ni(I), and Ni(III) but not in Ni(II) and Cu(III)?

In Fig. 3, Ψ_1 and Ψ_2 must have a large coupling matrix element to create stable pairing and make electron pair transfer possible. For cuprates (Fig. 3):

$$\mathrm{Cu_A(I) + Cu_B(III) \rightarrow Cu_A(II) + Cu_B(II) \rightarrow Cu_A(III) + Cu_B(I)} \tag{10}$$

The product of Slater determinants $\mathrm{Cu_A(I)} \times \mathrm{Cu_B(III)}$ integrated with $\mathrm{Cu_A(II)} \times \mathrm{Cu_B(II)}$ must be large and significant (Eq. (9)). In $\mathrm{Cu_A(I)} \times \mathrm{Cu_B(III)}$, both additional electrons in $\mathrm{Cu_A(I)}$ fill the $e_g(x^2 - y^2)$ orbital. Electron transfer to the empty e_g spin orbital of $\mathrm{Cu_B(II)}$ is possible. Transfer from $e_g(x^2 - y^2)$ on $\mathrm{Cu_A}$ with different spin to $\mathrm{Cu_B(II)}$ is also possible (Fig. 3a).

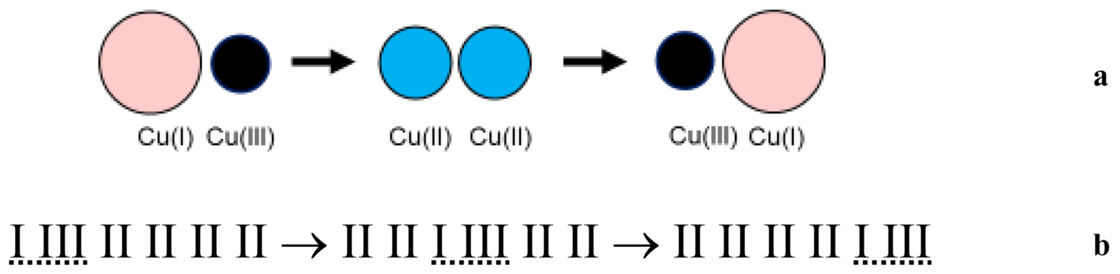

Fig. 3 Pair formation in **r**-space. **a** Two electrons move from A to B. **b** Pair flow in a chain from left to right involving three oxidation states

We now compare Eq. (10) to the corresponding Eq. (11) for nickelates:

$$\mathrm{Ni_A(I) + Ni_B(III) \rightarrow Ni_A(II) + Ni_B(II) \rightarrow Ni_A(III) + Ni_B(I)} \quad (11)$$

Ni_A(I) is a $3d^9$ system. Assuming that $e_g(x^2-y^2)$ is the highest occupied orbital (HOMO), the electron in the $e_g(x^2-y^2)$ can transfer to the empty $e_g(x^2-y^2)$ of Ni_B. The $e_g(x^2-y^2)$ on center Ni_A is now empty. Transfer of a second electron to $e_g(x^2-y^2)$ of Ni_B cannot be carried out unless we take it from the $e_g(z^2)$ orbital of Ni_A. The latter transfer needs energy which would lead to resistivity. Thus, an electron pair cannot be transferred from A to B in the Ni(II) case. Ni(II) cannot be SC.

Zhou et al. studied, however, an Ni(III) superlattice where Eq. (12) holds:

$$\mathrm{Ni_A(II) + Ni_B(IV) \rightarrow Ni_A(III) + Ni_B(III) \rightarrow Ni_A(IV) + Ni_B(II)} \quad (12)$$

Ni_A(II) is a $3d^8$ system and Ni_B(IV) a $3d^6$ system. The singly occupied $e_g(x^2-y^2)$ orbital ($3dz^2$ is unoccupied [1]) plays the same role as the occupied $e_g(x^2-y^2)$ in Cu(II). In the superlattice with NiO_2-MnO_2 planes in D_{4h} geometry, Ni(II) has singlet spin due to loss of degeneracy. Ni(IV) always has a closed $3d(t_{2g})^6$ subshell. Equation (12) is thus useful for pairing in a superlattice. $LaNiO_3$ becomes SC in a superlattice with $T_C \approx 3.5$ K. The other RNiO$_3$ systems collapse to an insulator as mentioned above [29, 30].

Also in the case of ref. [2, 3], the strategy was to find a similar nickelate perovskite structure as in the II-cuprates. Li et al. reduced $Nd_{1-x}Sr_xNiO_3$ to $Nd_{1-x}Sr_xNiO_2$ and doped the latter to x ≈0.2. Equation (13) replaces Eq. (12).

$$\mathrm{Ni_A(II) + Ni_B(0) \rightarrow Ni_A(I) + Ni_B(I) \rightarrow Ni_A(0) + Ni_B(II)} \quad (13)$$

The central oxidation state is Ni(I)-$3d^9$ as in Cu(II) with AS ground state. Ni(0) with $3d^{10}$ configuration is a spin singlet state, and Ni(II) is a spin singlet state in the superlattice. Ni(0) and Ni(II) are both spin singlet states in ref. [2]. Ni(I) in $LaNiO_2$ mimics Cu $3d^9$ well, as is the purpose. A problem is that the R ion La(III) is large and does not permit strong enough coupling. Li et al. [2] solved this problem by using Nd(III) instead of La(III) since Nd(III) is smaller than La(III). $Nd_{1-x}Sr_xNiO_2$ has as quite high critical temperature $T_C \approx 15$ K [2, 3].

We have thus explained the experimental results in both [1] and [2, 3]. The three important oxidation states are Ni(0)/Ni(I)/Ni(II) in [2, 3] and Ni(II)/Ni(III)/Ni(IV) in [1]. The spins are low spin on all nickel oxidation states from Ni(0) to Ni(IV) in the superlattice with D_{4h} local symmetry.

We conclude that the requirements of pairing and spin reduce severely the possibilities for SC in TMO. The 3-oxidation states rule for pairing implies that since Cu(II) is SC, the previous element in the periodic table, also with perovskite structure, can be SC for Ni(I) and Ni(III), but not for Ni(II). This agrees with the experimental findings so far.

There is also a 1-oxidation state rule for insulators. If a metal ion in a conducting chain of a metal oxide only possesses a single oxidation state, the conductivity is severely depressed since donors and acceptors are missing. An example is zinc for which Zn(II) is the only possible positive oxidation state [33]. Replacing Cu(II) by Zn(II) leads to canceling of a channel for ET. The same is the case for the ions that are used as dopants.

Finally there is the 2-oxidation states rule for ordinary metals already mentioned above. With oxidation states different in one unit on adjacent ions, Marcus ET is possible as we see from Eq. (2) above. If $E_a \rightarrow 0$ for $T \rightarrow 0$ K, the system goes from a quite normal insulator→metal, i.e., from **r**-space to **k**-space. A single hole or single electron on adjacent atoms is sufficient to form a metal but three successive spin singlet oxidation states are necessary to form a superconductor.

The theory given here is consistent with the results of refs. [1–3] that SC exists for oxidation states I and III for nickel, compared to Cu(II) for copper. This also shows that the Marcus model is a very useful model for metal–insulator transitions at doping.

6 The Importance of Coupling

In the first submitted version of this paper, the referee gracefully pointed out that in LaNiAsO the oxidation state is obviously Ni(II), though three oxidation states are necessary for SC. LaNiAsO is itself a superconductor for $T \sim 2.75$ K, in a compound where the oxidation state of Ni can only be Ni(II). However, the doped compound $LaNiAsO_{0.9}F_{0.1}$ shows sharp SC and specific heat jump at the critical temperature at $T_C \sim 3.8$. This hints that this pnictide is strongly coupled and is of the same type as the perovskite cuprates rather than a BCS superconductor [34]. The strong coupling is due to the much shorter distance between the directly coupled Ni(II) sites if bonded to the As(-III) ions as compared to the perovskites.

In a local system, bond lengths are different for different oxidation states in a mixed-valence system. In the limit of delocalization, after sufficient doping, the system is metallic without any bond length differences. This permits application of Bloch theory [35]. An experimental example is given in [32, 36] in the case of a doped Bi(III)-Bi(V) system.

The coupling between the Ni ions in the pnictides is sufficient to permit superconductivity and therefore no oxidation states with different bond distances can be detected.

7 Discussion and Conclusions

High T_C superconductivity takes us from the **r**-space of oxidation states to the **k**-space of metals. In the cuprates, the difference in bond length between Cu(I), Cu(II), and Cu(III) sites disappears when the system becomes metallic. In LaONiAs, due to direct bonding between the Ni ions and short NiAs distance in the NiAs complex, the undoped system is already metallic.

Metallic properties and bonding properties are complimentary in a sense of Bohr [37]. In a metallic system, no oxidation state differences can exist. In local theory, the bond lengths depend on the oxidation state of the metal ion. In the TMOs, the HOMOs are antibonding, hence shorter bonds for higher oxidation state.

In the transport chain of Fig. 3, the average oxidation state is Cu(II). In this transport, Cu(III) also plays a role as we see. Cu(III) is the so-called Zhang-Rice singlet, since in its spin singlet state, it was considered to have a special role in superconductivity. Actually it plays exactly the same role as Ni(II) in superconducting Ni(I) and Ni(III) oxides, i.e., a secondary role according to Eqs. (12) and (13) of importance for pair motion.

A quite simple theory for superconductivity in TMO may now be formulated for perovskite doped "Mott insulators" La_2CuO_4, La_2NiO_4, $LaNiO_3$, and $NdNiO_2$. In the **r**-space description, the only way to get conductivity by electron pairs is by disproportionation, Eq. (1) ($\hbar\omega = 0$). As soon as Cu(III) ions appear by doping, conductivity increases by orders of magnitude. The Mott parameter U becomes zero in photoconductivity spectra after some doping [7, 8]. At the same time, the TMOs become metallic.

Is there any difference between λ and U? According to Mott, U is the excitation energy of a vertical optical transition where one electron jumps to the next metal site with the same charge, without change of nuclear coordinates. λ is the same except that there is one electron less. Hence, $\lambda \approx U$. Both λ and U may collapse upon doping. The definition of U as on-site repulsion is not warranted. The curvature of the potential energy surfaces in the normal region is important in the Marcus model [12] and this leads to a low energy landscape in the far IR region.

Finally, the experimental data of [1–3] have been explained. We observe a connection between oxidation states and off-diagonal coupling matrix elements. Ni(I) and Ni(III) become SC in superlattices but not in the bulk. In the bulk, Ni(II) is high spin and therefore Ni(I) and Ni(III) cannot be SC. The coupling matrix elements to Ni(II) are equal to zero. Ni(II) cannot be SC even in a superlattice, due to the lack of coupling in Eq. (11).

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