General Rule and Materials Design of Negative Effective $U$ System for High-$T_c$ Superconductivity

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Based on the microscopic mechanisms of (1) charge-excitation-induced negative effective $U$ in $s^1$ or $d^9$ electronic configurations, and (2) exchange-correlation-induced negative effective $U$ in $d^3$ or $d^5$ electronic configurations, we propose a general rule and materials design of negative effective $U$ system in itinerant (ionic and metallic) system for the realization of high-$T_c$ superconductors. We design a $T_c$-enhancing layer (or clusters) of charge-excitation-induced negative effective $U$ connecting the superconducting layers for the realistic systems.

n order to realize a new-class of high-$T_c$ superconductors, we need to design and realize an itinerant (ionic and metallic) system carrying a large negative effective-correlation energy $U$ (NEU) with $U = E(N + 1) + E(N) - 2E(N) < 0$, where $E(N)$ is a total energy of an $N$ electron system. In addition to both Anderson’s mechanism\(^1\) induced by Jahn–Teller lattice distortion and the exchange-correlation-induced negative effective $U$ (ECI-NEU) mechanism,\(^2\) here, we propose a new microscopic mechanism of NEU caused by charge-excitation-induced NEU (CEI-NEU) from $s$- to $p$-orbital, or, $d$- to $s$-orbital in an ionic metal. NEU generally leads to a charge-density wave (CDW) by charge disproportionation, or superconductivity (SC) by attractive pairing-interaction, or a spin-density wave (SDW) by an exchange-correlation interaction. In this paper, we propose a general rule on chemical trends for NEU system in order to design a new-class of high-$T_c$ superconductor, which is always competing with a CDW or SDW state.

The total energy $E(N)$ shows normally a convexity due to the repulsive correlation energy ($U > 0$), guaranteeing stability of the $N$ electron system in the thermal equilibrium. If $(N - 1)$ electron system in $s^1$ (or $d^8$, or $d^9$) electronic configuration or $(N + 1)$ electron system in $s^2$ (or $d^{10}$, or $d^9$) electronic configuration becomes more stable than $N$ electron system in $s^1$ (or $d^8$, or $d^9$) electronic configuration by lowering $E(N + 1)$ through mixing of $s^2$ electronic configuration and charge excited states with $p$ electrons (or $d^{10}$ electronic configuration and charge excited states with $s$ electrons), or through the exchange-energy gain of $d^5$ electronic configuration,\(^3\) the $N$ electron system in $s^1$ (or $d^8$, or $d^9$) becomes NEU system due to the concavity of $E(N)$.

In \textit{ab initio} calculation, ECI-NEU mechanism is predicted in Si:Cr system\(^4\) and in (Ga,Mn)As system\(^5\) quantitatively. In the reaction of $2s^1 \rightarrow s^0 + s^2$ (or $2d^9 \rightarrow d^8 + d^{10}$, or $2d^8 \rightarrow d^7 + d^9$), we can expect a charge disproportionation and insulating CDW. However, if we can realize an itinerant NEU system upon $p$- or $n$-type doping or under the applied ultra-high pressures by destabilizing CDW or SDW, we can stabilize a superconducting state caused by electron pairing through attractive-carrier dynamics.

Indication of NEU system appears as the missing oxidation states in experiments. When we look at a Cr\(^0\) atom, we see the missing state in the $3d^4$ electronic configuration, where $3d^4s^1$ becomes more stable than $3d^4s^2$ due to the exchange-correlation energy gain in $d^3$. When a free atom is placed in polarizable host materials such as oxides or semiconductors, the Coulomb interaction, responding to long-wave length (mono-pole) screening, is reduced far more than the exchange-correlation interaction (multi-pole screening).\(^4\) This has been demonstrated theoretically and experimentally,\(^5,6\) as is called the Haldane and Anderson mechanism.\(^6\)

Katayama-Yoshida and Zunger\(^7\) proposed that localized centers sustaining local magnetic moment can show NEU behavior, when the exchange (or, in general, many-electron correlation) interactions outweigh the strongly reduced Coulomb repulsions in the covalent materials such as oxides or covalent semiconductors. This NEU mechanism can explain missing oxidation states in chemistry,\(^8,9\) e.g., while both Mn\(^{3+}(d^7)\) and Mn\(^{4+}(d^8)\) are observed in MgO:Mn and CaO:Mn, the Mn\(^{3+}(d^7)\) center is missing;\(^10\) also in (Ga,Mn)As system, the Mn\(^{3+}(d^7)\) center is missing.\(^11\) If we can realize itinerant ECI-NEU system with destabilizing the ferromagnetic SDW, we have a possibility to stabilize the superconducting state in $d^4$ (or $d^9$) by ECI-NEU. However, SDW is generally more stable than a superconducting state in Mn\(^{3+}(d^7)\) with large exchange-correlation energy gain in (Ga,Mn)As or perovskite manganites.

Therefore, for $3d$ transition atoms in the condensed matter, we can expect the ECI-NEU in $d^4$ (or $d^9$).\(^2\) ECI-NEU causes the missing oxidation state in $d^4$ (or $d^9$) through the charge disproportionations or dynamical charge fluctuation mediating even a superconducting state in the reaction of $2d^4 \rightarrow d^3 + d^5$ ($U < 0$) [or, $2d^6 \rightarrow d^5 + d^7$ ($U < 0$)]. The candidates of ECI-NEU system are listed in Table I.

We have another microscopic mechanism of NEU system in $s^1$ or $d^3$. Here we may refer to the observed chemical trends of first ($A^0 \rightarrow A^+ + e^-$), second ($A^+ \rightarrow A^{2+} + e^-$), and third ($A^{2+} \rightarrow A^{3+} + e^-$) ionization energies of free atoms in the second, third, fourth, and fifth period in the periodic table. We find that the ionization energy of $s^1$ for $2s$, $3s$, $4s$, and $5s$-orbitals shows the minimum suggesting instability of $s^1$, and that $s^2$ show always the peak suggesting stability of the closed-shell $s^2$ electronic configuration.\(^12\)

In experiment, the existence of the missing oxidation states of ions such as Ti$^{2+}$($6s^1$), Pb$^{3+}$($6s^1$), Hg$^{2+}$($6s^1$), and Bi$^{4+}$($6s^1$) in the periodic table is well-known.\(^13,14\) These atoms indicate NEU nature, where following charge disproportionation occurs in the insulating compounds;

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Table I. (a) Exchange-correlation-induced negative effective \( U \) ions for \( d^4 \) and \( d^6 \) electronic configuration, and (b) charge-excitation-induced negative effective \( U \) ions for \( d^2 \) electronic configuration.

| Charge | Negative effective U center | Materials |
|--------|-----------------------------|-----------|
| +2     | Zn\(^{2+}\) (4s\(^2\)), Ca\(^{2+}\) (4s\(^2\)) | n-type doped ZnO, CaO, MgO, BeO, CdO, BaO, SrO, HgO |
| +2     | In\(^{3+}\) (5s\(^1\)), Al\(^{3+}\) (3s\(^1\)), B\(^{3+}\) (2s\(^1\)), Y\(^{3+}\) (5s\(^1\)) | n-type doped In\(_2\)O\(_3\), Al\(_2\)O\(_3\), Be\(_2\)O\(_3\) |
| +3     | C\(^{3+}\) (2s\(^2\)), Si\(^{3+}\) (3s\(^2\)), Ti\(^{3+}\) (4s\(^1\)), Zr\(^{3+}\) (5s\(^1\)) | n-type doped CO\(_2\), SiO\(_2\), TiO\(_2\), ZrO\(_2\), GeO\(_2\), SnO\(_2\), PbO\(_2\), p-type doped GeO, SnO, PbO |
| +4     | N\(^{4+}\) (2s\(^1\)), P\(^{4+}\) (3s\(^1\)), V\(^{4+}\) (4s\(^1\)), Nb\(^{4+}\) (5s\(^1\)), As\(^{4+}\) (4s\(^1\)), Sb\(^{4+}\) (5s\(^1\)) | n-type doped VO\(_2\), NbO\(_2\), AsO\(_3\)O\(_2\), NaAsO\(_3\), SnO\(_2\)O\(_10\), B\(_2\)O\(_5\), Na\(_2\)O, As\(_2\)O\(_3\), SnO, PbO |
| +5     | O\(^{5+}\) (2s\(^1\)), S\(^{5+}\) (3s\(^1\)), Cr\(^{5+}\) (4s\(^1\)), Mo\(^{5+}\) (5s\(^1\)), Se\(^{5+}\) (4s\(^1\)), Te\(^{5+}\) (5s\(^1\)), Po\(^{5+}\) (6s\(^1\)) | n-type doped MoO\(_3\), SeO\(_2\), TeO\(_2\), p-type doped MoO\(_2\), H\(_2\)SeO\(_4\), TeO\(_2\) |
| +6     | F\(^{6+}\) (2s\(^1\)), Cl\(^{6+}\) (3s\(^1\)), Mn\(^{6+}\) (4s\(^1\)), Tc\(^{6+}\) (5s\(^1\)), Br\(^{6+}\) (4s\(^1\)), I\(^{6+}\) (5s\(^1\)), At\(^{6+}\) (6s\(^1\)) | n-type doped H\(_2\)O\(_2\), HIO\(_2\), KBrO\(_3\), MnO\(_2\), HClO\(_4\), p-type doped I\(_2\)O\(_5\), HIO\(_3\), NaBrO, HClO\(_3\) |
avoid anti-ferromagnetic SDW upon p- or n-type doping with the itinerant system. For cuprate high-\( T_c \) superconductors, such as \( \text{La}_{2-x} \text{Sr}_x \text{CuO}_4 \) or \( \text{YBa}_2 \text{Cu}_3 \text{O}_7 \), the ground state of undoped system is anti-ferromagnetic and charge-transfer insulator caused by the super-exchange interactions in the CuO\(_2\) layer. It may be possible that the superconductivity is caused (or enhanced) by CEI-NEU in the Cu\(^{2+}(3d^9)\) in the itinerant system by destabilizing the anti-ferromagnetic SDW ordering upon p-type doping such as C\(_{\text{in}}\) in the conducting-covalent large molecules or clusters, such as \(\text{C}_{25}\). Table II with partial ionization caused by the super-exchange interaction and the superconductivity caused by CEI-NEU in Cu\(^{2+}(3d^9)\) system. The possibility of NEU-induced superconductivity caused by charge-fluctuation-induced NEU is proposed and discussed by Varma, combined with the missing oxidation states in BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) and BK\(_{1-x}\)Bi\(_x\)O\(_3\). \(^{17}\)

For the cuprate high-\( T_c \) superconductors such as \(\text{La}_{2-x} \text{Sr}_x \text{CuO}_4\), \(\text{YBa}_2 \text{Cu}_3 \text{O}_7\), \(\text{Bi}_2 \text{Sr}_2 \text{Ca}_x \text{Cu}_2 \text{O}_{10}\), (Hg,Re)-Ba\(_x\)Ca\(_{1-x}\)Cu\(_2\)O\(_y\), HgBa\(_2\)Ca\(_2\)Cu\(_2\)O\(_y\), Tl\(_2\)Ba\(_2\)Ca\(_2\)Cu\(_2\)O\(_y\), we may have an additional-pairing mechanism in the \( T_c \)-enhancing layers which is caused by the CEI-NEU in the electron-doped BaO, SrO, BiO, TIO, Y\(_2\)O\(_3\), PbO or HgO layers upon the oxygen-vacancy doping. For new-type superconductors such as MgB\(_2\) \(^{18}\) and CaSi\(_2\), it is also possible to expect an additional pairing mechanism for \( T_c \)-enhancement caused by the CEI-NEU in the \( s^\pm \) electronic configurations of atoms or ions listed in Table II with partial ionization caused by the \( \pi \)-orbital hybridization perpendicular to the sphere or cluster surfaces in the conducting-covalent large molecules or clusters, such as C\(_{60}\), zeolite, or, [Ca\(_{24}\)Al\(_{20}\)O\(_{64}\)]\(^{4+}(4e^-)\).

Recently, it was discovered a new-type high-\( T_c \) superconductors in the Ni- and Fe-based oxypnictides, such as \(\text{La}(\text{O}_{1-x} \text{F}_x)\)FeP (\( T_c = 5 \) K), \(^{19}\) LaONiP (\( T_c = 3 \) K), \(^{19}\) La\(_{(1-x)}\)Fe\(_x\)As (\( T_c = 26 \) K), \(\text{Gd}(\text{O}_{1-x} \text{F}_x)\)FeAs (\( T_c = 53.5 \) K), \(\text{Nd}(\text{O}_{1-x} \text{F}_x)\)FeAs (\( T_c = 55 \) K), \(\text{Sm}(\text{O}_{1-x} \text{F}_x)\)FeAs (\( T_c = 43 \) K), \(\text{LaO}_{0.85}\text{Sr}_{0.15}\)FeAs (\( T_c = 25 \) K), \(\text{La}(\text{O}_{1-x} \text{F}_x)\)FeAs (\( T_c = 46 \) K at \( P = 4 \) GPa), and \(\text{Ba}_{1-x} \text{K}_x\)Fe\(_2\)As\(_2\) (\( T_c = 38 \) K). These new-type superconductors also contain CEI-NEU ions, such as La\(^{2+}(6s^1)\), Nd\(^{2+}(6s^1)\), Gd\(^{2+}(6s^1)\), and Sm\(^{2+}(6s^1)\), with the electron-doped LaO, GdO, NdO, and SmO-layers by F-donor doping or oxygen-vacancy-donor doping. Based upon our materials design as discussed above, we have a possibility to enhance the \( T_c \) by using another layers of NEU ions as listed in Table II. These are all promising candidates for \( T_c \)-enhancing layers by CEI-NEU. The oxypnictides contain Fe\(^{2+}(3d^6)\) which is ECI-NEU system as was discussed above. We should also try the candidates of ECI-NEU system such as listed in Table I.

We design a new-class of NEU system for the realization of new-class of high-\( T_c \) superconducting materials by controlling (i) CEI-NEU in \( s^\pm \) (or \( d^\pm \)) electronic configurations, and (ii) ECI-NEU in \( d^\pm \) (or \( d^\pm \)) electronic configurations. Here, we have proposed the general rules and chemical trends of NEU system for the realization of high-\( T_c \) superconductivity in real materials. We also proposed the materials design for the realization of high-\( T_c \) superconductivity based on the general rules and chemical trends comparing with the available experimental data.

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