

Electronic states of Cu in cuprate superconductors: Atomic model

R. Dagys and G.-J. Babonas

Semiconductor Physics Institute, LT-2600 Vilnius, Lithuania

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The electronic states of Cu in crystals were investigated in the framework of the Slater model of neutral atoms in crystals. It was shown that the closeness of divalent $3d^94s^2$ and monovalent $3d^{10}4s$ states of Cu and the strong dependence of their mutual arrangement on the crystal field strength is the distinctive feature of Cu among transition metal elements and other neighbors in Periodic Table. These Cu states show the tendency to cross in Cu-O planes of cuprate superconductors, when superconducting composition is approached.

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It is generally accepted that Cu-O planes represent the main structural element responsible for superconductivity in cuprates. Therefore, it is natural to assume that superconductivity is connected with some particular features in the electronic structure of Cu-O planes. However, theoretical models meet large difficulties because of well-known complications in the determination of the electronic structure of the systems, the properties of which are caused by differently localized and differently correlated electrons. Various forms of the model Hamiltonian have been used to describe the physical properties of such materials. The different values of Hamiltonian parameters and the large variety of superconductivity mechanisms proposed actually reflect these complications.

This problem can be simplified by taking into account that substitution of Cu by other atoms usually leads to suppression of superconductivity. Therefore, it may be assumed that Cu is the key element in superconductivity of cuprates and that the specific features of the Cu-O properties are caused mainly by the distinctive features in the electronic structure of Cu atoms. However, even specific features of Cu are difficult to reveal by using the ionic model, which is usually the starting model for various theories.

In the present paper, the electronic states of Cu in cuprate superconductors are considered on the basis of the regularities determined in previous experimental and theoretical studies on rare earth (RE) and transition metal compounds and taking into account the correlations observed in cuprates. The specific features of Cu are shown to be clearly revealed when using the Slater model for neutral atoms in crystals,¹ which has been successfully applied to the study of similar problems in RE compounds.^{2,3} From this model, it follows that with respect to other transition metal elements and other neighbors in the Periodic Table the distinctive features of Cu important for superconductivity are the closeness of the monovalent and divalent states of Cu in crystals and a strong dependence of their mutual arrangement on the crystal field strength and, correspondingly, on the composition of the crystal. The tendency of monovalent and divalent states of Cu in Cu-O planes to cross, i.e., a possible appearance of intermediate valence state, when approaching the superconducting composition, will be shown. The results obtained may be considered as an additional argument in favor of a charge-transfer resonance fluctuation mechanism for superconductivity.⁴

The Cu atom is similar to some RE elements in its possibility to take various valence states in different crystals. In the case of RE elements, this feature is related to the closeness of the different valence states $4f^{N-x}5d^x6s^2$ ($x=0,1,2$) in crystals due to the relatively small energy intervals E_{4f}^{5d} between these states in free atoms and their decrease in crystals because of the crystal field splitting of $5d$ levels.^{2,5} As a result of this closeness, the mutual arrangement of different valence states strongly depends on crystal field strength and, correspondingly, on crystal structure and composition. For example, in thulium chalcogenides TmX ($X=S, Se, Te$), Tm remains in the divalent state $4f^{13}6s^2$, as it is in a free atom, only in the case of the weakest crystal field, i.e., in TmTe.⁶ In TmS, in which the crystal field is strongest among TmX compounds, Tm is in a trivalent state,⁷ which is separated from the ground divalent state by the interval $E_{4f}^{5d}=1.63$ eV (Ref. 8) in free Tm atoms. In TmSe, which is intermediate among TmX compounds regarding crystal field strength, its specific properties are related to the crossing of $4f^{12}5d6s^2$ and $4f^{13}6s^2$ states in crystal, i.e., to the intermediate valence of the Tm atom.⁶

The crystal field splitting of $5d$ levels and the character of the mutual arrangement of different valence states of RE atoms in crystals may be simply changed by external pressure as well. A well investigated example is SmS, in which the trivalent state $4f^55d6s^2$ of Sm is very close to the ground divalent state $4f^66s^2$. An increase of $5d$ level splitting due to an increase of pressure leads to a decrease of interval between these states and to their crossing at $p=6.5$ kbar.⁵ The famous ‘‘black’’ to ‘‘gold’’ transition in SmS is interpreted as a result of this crossing.⁵ The similar transition occurs in $Sm_{1-x}Gd_xS$ at $x\approx 0.15$ due to internal pressure originated by the substitution of Sm by Gd ions of smaller size and larger charge.

Therefore, the dependence of valence states of RE ions on various factors in crystals may be interpreted by using a simple atomic model, in which the influence of the rest of crystal is taken into account only by the crystal field acting on the $5d$ states. It should be emphasized that in considering this problem, the E_{4f}^{5d} values for neutral atoms should be used, i.e., the model of neutral atoms in crystals should be applied, though RE compounds are usually treated as ionic crystals. As has been shown in Refs. 2 and 3, the outer elec-

trons of metal atoms in ionic crystals remain at the same radial distances as in neutral atoms, reflecting the well-known fact that ionicity is the result of charge overlap rather than charge transfer (see, for example, Ref. 1).

In the model of neutral atoms in crystals, the question of Cu valence in crystals can be considered similarly as in the case of RE compounds. As is well known, the ground configuration of the neutral Cu atom is $3d^{10}4s$. The Cu atomic radius obtained by Hartree-Fock calculations and corresponding to the maximum of charge density for the outer $4s$ electron in such a configuration is $a_{4s}=1.36$ Å. Taking into account the correspondent radius $a_{2p}=0.46$ Å of a neutral oxygen atom, the sum $a_{4s}+a_{2p}=1.82$ Å agrees well with the experimental Cu-O distance in the compounds, in which Cu is monovalent. For example, in Cu_2O , this distance is equal to 1.84 Å (Ref. 1), and in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound the distance between the neighboring Cu(1) and O(4) atoms is 1.80 Å.⁹ Such good agreement can be interpreted as one of the arguments for the application of the neutral atoms in crystals model in the studies of Cu states in Cu-O systems. As in the case of RE compounds,^{2,3} a weighty argument in favor of this model is the good agreement between experimental intra-atomic transition energies in crystals and those which follow from the model. A proper example is the peak observed at 4.1 eV in the optical spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds with oxygen deficiency which is assigned to $3d \rightarrow 4p$ transitions in the Cu^+ ion.¹⁰ In the case of the free Cu^+ ion, the lowest excitation energy from the $3d^{10}$ state to the $3d^9 4p$ state is equal to 8.2 eV.¹¹ This large difference from experimental value can hardly be explained in the frame of the ionic model. In the model of neutral atoms, i.e., taking into account that the $4s$ electron in crystals still remains on the Cu atom, the lowest excitation energy from the $3d^{10}4s$ to the $3d^9 4p 4s$ state in a free Cu atom is 5.5 eV.¹¹ This value is only 1.4 eV higher than the experimental one and the obtained difference can be easily explained by a reduction of the lowest $3d^9 4p 4s$ state energy in a crystal due to the splitting of the $3d^9$ level in a crystal field.

Some other arguments for application of the model of neutral atoms in crystals are given in studies¹² of $3d$ states in transition metal oxides.

By analogy with RE compounds, it is thus easy to explain why Cu can exist in crystals in a monovalent as well as in divalent state. In a free Cu atom, the divalent state $3d^9 4s^2$ is located only 1.39 eV higher than the monovalent state $3d^{10}4s$.¹¹ Due to splitting of the $3d^9$ state in crystal, the energies of the lowest $3d^9 4s^2$ and $3d^{10}4s$ states come close together and can be inverted in a stronger crystal field. From this point of view, the situation is similar to that for Tm in TmX .

The correlation between the Cu valence and crystal field strength does really exist. For example, from the point charge crystal field model, it follows that for similar Cu-O distances R , the energy decrease of the ground level in $3d^9$ configuration is stronger by $\alpha_4/3$ in the crystal field of square coordination than in the linear coordination ($\alpha_4 = Z^* e^2 \bar{r}^4 / R^5$ is the crystal field parameter and \bar{r} is the mean radius of $3d$ electron). This is in agreement with Cu divalent states in square coordination [Cu in CuO or Cu(2) in $\text{YBa}_2\text{Cu}_3\text{O}_6$] and in monovalent states in linear coordination [Cu in Cu_2O or Cu(1) in $\text{YBa}_2\text{Cu}_3\text{O}_6$]. Similarly, the

crystal field in octahedral coordination is stronger than that in tetrahedral coordination, consistent with the fact that Cu is divalent in Ln_2CuO_4 and monovalent in, for example, CuX ($\text{X}=\text{Cl}, \text{Br}, \text{J}$).

The closeness of divalent and monovalent states of Cu in crystals is the distinctive feature of Cu among transition metal elements, in which the divalent state in crystals corresponds to a significantly lower energy than in the monovalent state. As the superconductivity of cuprates is suppressed by the substitution of Cu with other transition metal elements, this feature is assumed to be important in the superconductivity phenomenon. This assumption is supported by different effects on superconductivity by Cu substitution with silver and gold,¹³ when the superconductivity is suppressed and unchanged, respectively. The divalent state $4d^9 5s^2$ of silver in crystal occurs significantly higher than the monovalent state due to the large 3.7 eV interval¹¹ between these states in a free atom. In contrast, these states in gold are located similarly as in Cu, i.e., the $5d^9 4s^2$ state is only 1.14 eV higher than $5d^{10}4s$.¹¹

As divalent and monovalent Cu states in crystals are energetically close to each other, it is reasonable to assume the possibility of their crossing when the composition of a crystal is changed. Such a tendency clearly manifests itself, considering the Cu(2) states in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ when saturated by oxygen. At high oxygen deficiency, Cu(2) atoms are in a divalent state due to a strong crystal field created mainly by neighboring oxygens O(2) and O(3). However, going from $x \approx 0$ to $x=1$, a drastic reduction of the distance between Cu(2) and the apical oxygen O(4) takes place.⁹ The decrease works faster in the region of transition to superconducting composition and results in an abrupt decrease of the crystal field and an increase of the divalent state energy. [In the point charge model, the contribution of additional oxygen O(4) increases the energy of the lowest $3d^9$ level by the quantity $\Delta E = (6/21)\bar{\alpha}_2 - (1/21)\bar{\alpha}_4$, where $\bar{\alpha}_2$ and $\bar{\alpha}_4$ are crystal field parameters corresponding to the O(4) atom]. The importance of the influence of apical oxygen on Cu(2) states is justified by the often emphasized relationship between superconductivity and location of apical oxygen (see, for example, Ref. 14).

A similar situation occurs in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with the substitution of Sr for La, when two apical oxygen atoms approach Cu,¹⁵ hence decreasing the crystal field strength. In $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the second neighbors should possibly contribute to the decrease of the crystal field approaching the superconducting composition. Therefore, an increase of the distance between Cu(2) and Y, Ba atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, as well as the heterovalent substitution by the smaller charge ion in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, should be taken into account.

The assumption of the crossing of divalent and monovalent states of the Cu atom in the Cu-O planes is supported by further observations. In fact, one can note the similarity between the changes of the properties of cuprate in the normal state, when the superconducting composition is approached, and those of RE compounds, when they are transferred to the intermediate valence state. For example, a very close similarity exists between dependences of charge carrier concentrations n on composition x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Sm}_{1-x}\text{Gd}_x\text{S}$. In both crystals, n is linearly proportional to

x in the semiconductor region. This dependence becomes significantly stronger in the region of transition to the superconducting composition in cuprates¹⁶ and to intermediate valence state in sulfides.⁵ In both cases, the enhancement of this dependence can be related to the crossing of “nonmetallic” states, $3d^9 4s^2$ in Cu and $4f^6 6s^2$ in Sm, with “metalliclike” states, $3d^{10} 4s$ in Cu and $4f^5 5d 6s^2$ in Sm. On the other hand, common features of the changes in magnetic properties are noted in cuprates, when passing to a superconducting state, and in RE compounds, when the intermediate valence state is achieved at the crossing of magnetic and nonmagnetic states of RE atoms.⁵

It should be noted that the high-temperature Meissner effect observed in pressure-quenched CuCl (Ref. 17) does not contradict the model of the Cu intermediate valence state in superconducting composition. In CuX (X=Cl, Br, J) compounds, the largest crystal field splitting occurs in CuCl, i.e., in the latter case the divalent state $3d^9 4s^2$ is at the closest distance to the monovalent state $3d^{10} 4s$. It is possible that the bond lengths in Cu-Cl tetrahedra are shorter or that the tetrahedra are distorted in the samples obtained in such extreme conditions. Both of these factors enhance the crystal

field and cause the divalent and monovalent states to approach each other.

Detailed experimental analysis of the dependence of superconductivity on the changes of the crystal field strength, for example, at the substitutions of basic elements, should give experimental evidence of the crossing of Cu states in the superconducting cuprates. Finally, it should be noted that so-called “charge-transfer resonance” fluctuations between anion and cation sublattices were concluded⁴ to be one of the more reliable superconductivity mechanisms determined by the selection of the relative parameter values in effective Hamiltonian in the framework of an extended Hubbard model. As it was noted in Ref. 18, these fluctuations are, in fact, between the $p^6 + d^9$ and $p^5 + d^{10}$ states. As a matter of fact, the latter two ionic states correspond to divalent and monovalent Cu states in the model of neutral atoms in crystal. Therefore, the specific features of Cu discussed in the present work can be considered as an additional argument in favor of this superconductivity mechanism.

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