The Interpretaion of Conventional Superconductivity on the Basis of Hypothesis of Small Polaron

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ABSTRACT

The mechanism of conventional superconductivity is well-known to be able to be explained on the basis of BCS theory which is based on the ambiguous correlation between a normal state and superconducting state of metals. The theory however cannot extend to the unconventional superconductivity such as high temperature superconductivity (HTS). We propose in this work the small polaron hypothesis for the conventional superconductivity instead of BCS theory, which may be possible to extend to the mechanism of HTS. The small polaron hypothesis could explain the strong correlation between the superconductivity and hydrogen overpotential of soft Hg, Pb metals, precious Pt and Au metals. The result of this work will bridge between a superconducting material and nanotechnology.

Keywords: conventional superconductivity mechanism, small polaron, hydrogen overpotential

1 INTRODUCTION

A polaron theory of a simple ionic crystal such as NaCl has been studied for a long time since the seminal work of Fröhlich [1]. The lattice deformation by a moving electron in a conduction band is thought to form a quasi-particle , a polaron. If the size of the polaron is smaller than a lattice constant, it is called a small polaron in contrast with a large polaron. A small polaron theory has been applied to a high temperature superconducting oxide in order to explain the superconducting mechanism, in which Jahn-Teller small polaron is usually assumed in order to stress the effect of lattice deformation on a hole carrier [2]. Furthermore it is considered that a small bipolaron condenses in a superconducting state. On the other hand the mechanism of superconductivity of conventional metals such as Hg and Pb is explained by a famous BCS theory [3], in which a Cooper pair, a large bipolaron, condenses in the superconducting state.

The author reported on the mechanism of the mediated electrochemical dissolution of semiconducting plutonium dioxide (PuO_2) micro-particle in the previous conference , Nanotech 2010 [4]. In the mechanism it was proposed the formation of a surface small polaron is of a great importance in the oxidative and reductive dissolution of PuO_2, respectively. Furthermore it was shown that a covalent bonding on the basis of a molecular orbital theory is much more important than an ionic bonding of PuO_2 in the dissolution process. This result should mean the formation of a small polaron by Jahn-Teller molecular orbital energy in the ionic metal oxide. By extending the idea to the conventional metal we could assume the formation of Jahn-Teller small polaron in the mechanism of the superconductivity because a metallic bonding is of a covalent nature.

2 DISCUSSION

2.1 Mechanism of Mediated Electrochemical Dissolution of PuO_2

The mechanisms of the oxidative and reductive dissolution of PuO_2 were previously discussed [4]. The main points of the mechanism will be summarized as follows.

1) The rate-controlling step of the dissolution of PuO_2 is an interfacial electron transfer between solid tetravalent plutonium Pu^{4+}(s) and aqueous oxidizing, or reducing metal ions respectively.

2) The covalent bonding of $[PuO_4]^{4-}$ cluster of D_{2h} point group symmetry in the (110) plane of the cubic lattice is ruptured by electron transfer reaction. Bonding electrons of HOMO are transferred in the case of oxidative dissolution. On the other hand an electron transfer to the virtual orbital, LUMO, is decisive in the case of the reductive dissolution.

3) Surface small polarons, hole and electron are formed during the oxidative and reductive dissolution respectively.

2.2 Interpretaion of Hydrogen Overpotential in Terms of Surface Small Polaron Model

The mechansim of hydrogen overpotential is usually discussed by means of Tafel, Volmer and Heyrovsky mechanisms. We will, however, discuss the hydrogen overpotential on the basis of the hypothesis of small polaron at the surface of cathode metal by extending the idea of the dissolution mechanism of PuO_2.

$$H^+ + e^{-*} \rightarrow H \quad (1)$$

, where H^+ and H are aqueous proton and hydrogen atom, respectively. e^{-*} is a surface small polaron of metal. That is, the hydrogen overpotential depends on the self-energy of surface small polaron which could differ greatly from metal to metal.

2.3 The Correlation between Hydrogen Overpotential and Superconductivity of Conventional Metal

Soft metals Hg and Pb of higher hydrogen overpotential, 0.78 and 0.64 V respectively are good superconducting metals T_c = 4.15, 7.19 K. On the other hand, precious metals Pt and Au of much lower hydrogen overpotential are not superconducting. That is, it may be possible to discuss the superconducting mechanism of conventional metal in terms of a small polaron. A small polaron is considered to conduct in an ionic solid by a tunnelling mechanism in a lower temperature range, whereas it conducts by a hopping mechanism in a higher temperature range. As the superconducting state arises at a lower temperature in general, the resonant tunnelling mechanism of a small polaron should play a predominant role in the superconducting state. Our model for superconductivity is completely different from the conventional theory of superconductivity in which the condensation of Cooper pair is decisive. We assume a single small polaron in the superconducting state of conventional metal. Our model will be extended to HTS oxides. We does not, however assume the bipolaron in that case as well. Only a single polaron is considered to be decisive for the superconducting state of metal oxide such as copper oxides.

2.4 The Correlation between Hardness and Superconductivity of Metal

The small polaron model for the conventional superconductivity strongly suggests that the local lattice deformation of metal leads to the formation of the small polaron. The local lattice deformation of metal crystal lattice must mean the deformation of M-M covalent bonding. Thus the superconductivity may be related to the hardness of metal, which is usually interpreted by a covalent bonding of metal. The experimental fact that the soft non-transition metals such as Hg, Pb and Sn(T_c = 3.72 K) are superconducting will not be in conflict with our small polaron hypothesis.

3 CONCLUSION

There has been no theory yet by which we can explain all of superconducting behaviour. A single small polaron hypothesis may be one candidate for such a consistent theory for superconductivity. The superconductivity of the nanometre-sized quasi-two-dimensional film may also be explained on the basis of that hypothesis.

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APPENDIX

This study is an experimental rather than a theoretical kind of one. The author, however would like to give some remarks on the fundamental theory of superconductivity. The conventional theory of superconductivity is well-known to be in consistent with the London equation which can explain phenomenologically the Meissner effect and replace the classical Ohm`s law. However, our small polaron model for the conventional superconductivity is based on Ohm`s law. That is, we will not be able to assume the exact zero for the resistivity in a superconducting state because Ohm`s law is mathematically indefinite at V=0 and R=0. Although the Ohm`s law is a kinetic law, it is not in conflict with the third law of thermodynamics because the resistance of pure metal becomes zero only at the absolute zero of temperature. On the other hand the conventional theory of superconductivity, which is based on the second law of thermodynamics, is ambiguous as to whether the theory is in consistent with the third law of thermodynamics because the theory assumes the exact zero of resistivity in a superconducting state.