Bull. Inst. Chem. Res., Kyoto Univ., Vol. 59, No. 1, 1981

Estimation of Superconducting Effect on the Decay Rate of ^{99m}Tc

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Received December 5, 1980

The upper limit of the relative change in the decay rate of ^{99m}Tc caused by the superconducting transition is estimated by applying a model developed for estimation of the chemical effect. In this model, one-electron wave function is calculated under Hartree-Fock-Slater type atomic potential, where the effect of different environmental condition is taken into account simply through the perturbation in the exchange potential. The upper limit of the superconducting effect was found to be $\sim 10^{-7}$, being consistent with our experimental result.

KEY WORDS: Superconductor/ Tc/ Decay rate/

The isomer ^{99m}Tc ($T_{1/2}$=6.0 h) is the second excited state decaying to the ground state ^{99}Tc ($T_{1/2}=2.12\times 10^5\ y$) through a cascade nuclear transition, of which the transition energies are 2.17 and 140.5 keV, respectively. The isomeric transition of ^{99m}Tc to the first excited state has an E3 character and proceeds almost completely by internal conversion, where the conversion can take place only in the M and N shells due to its low transition energy. This indicates that the change in the conversion probability (or decay rate λ_{Tc}) may be observable when the isomer is in different environmental conditions. In fact, various attempts to observe the external influence on λ_{Tc} have been performed by many workers.[1)]

In 1958, Byers and Stump[2)] compared the decay constant of ^{99m}Tc in the normal state and in the superconducting state, and found the relative increase in the decay rate, $\Delta\lambda/\lambda_{Tc}$, for the superconducting state is $(6.4\pm 0.4)\times 10^{-4}$. Olin and Bainbridge[3)] studied a similar effect in ^{90m}Nb and found the relative decrease in its decay rate of $(-19.5\pm 5.5)\times 10^{-4}$ for the superconducting effect. They assigned the difference in sign to the different modes of transitions in ^{99m}Tc (E3) and ^{90m}Nb (M2). These rather large superconducting effects on decay rate are very interesting, because as suggested in ref. 3, superconductivity may have some effect on the core electrons, at least in the transition metal region. They suggested that the reduced isotope effect of transition metals might be in some relation to the superconducting effect on the core electrons. According to the BCS theory,[4)] only electrons near the Fermi surface are concerned to the superconducting state. Therefore, if appreciable effect of the superconductivity exists on the core electrons, a new interaction other than the electron-phonon coupling is inferred for the superconducting transition. With an intention to see this effect, we examined the superconducting effect on λ_{Tc}, but we found no effect within an accuracy of our experiment.[5,6)] Our result is ap-

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parently inconsistent with that of Byers and Stump.

In this paper, rough theoretical estimation of the superconducting effect on λ_{Tc} is presented. The electronic state of Tc atom in superconducting state is evaluated on the basis of the BCS theory, and probable difference in the atomic potential between superconducting and normal states is estimated.

The present consideration is made on the analogy of the model used for the estimation of the chemical effect on λ_{Tc}.[7] In this model, one-electron wave function is calculated under Hartree-Fock-Slater (HFS)-type atomic potential. The different chemical conditions are taken into account simply through the perturbation in the exchange potential, which is proportional to the cubic root of the electron density. According to the estimation of the chemical effect, it has been revealed that the delocalization of $4d$ electrons and the squeezing of $4p$ electrons are the most responsible for the change in λ_{Tc}, which is of the order of $10^{-3}\sim10^{-4}$.

Since the theory of superconductivity is constructed on the basis of electron-phonon interaction in macroscopic scale, it is not suitable to treat individual atoms. However, assuming that the electron-phonon interaction changes the atomic potential, the change in the electronic state of an atom at the superconducting transition can be estimated on the analogy of the estimation of the chemical effect on λ_{Tc}.

In the BCS theory the superconducting ground state is built up by pairs of electrons (Cooper pair) which mutually interact within a coherent distance of the order of thousand atomic distances. An exchange of virtual phonon gives, on average, an attraction to the electrons within a certain energy interval around the Fermi level, and this attractive force may under certain circumstances dominate over the screened Coulomb repulsion. The resulting attractive interaction between electrons is in general very small.

In the original BCS theory, the attractive interaction was approximated by a small constant value, $-V$. Furthermore BCS assumed the Cooper pairs are formed only in the electrons within an energy interval of $2\hbar\omega_0$ below and above the Fermi level. Here, $\hbar\omega_0$ is an average phonon energy, approximately equal to the Debye energy. The Cooper pairs formed in this way come to have the character of Bose particles, and are condensed into the ground state in a macroscopic scale. Then the total free energy of the electron system is reduced, and an energy gap Δ appears in excitation spectrum. According to the BCS theory, Δ in the limit of 0 K is given as

$$\Delta = 2\hbar\omega_0 \exp[-1/N(0)V], \tag{1}$$

and the superconducting transition temperature T_0 is expressed similarly by

$$k_B T_0 = 1.14\hbar\omega_0 \exp[-1/N(0)V], \tag{2}$$

where $N(0)$ is the density of states at the Fermi level for electrons of one spin orientation and k_B is the Boltzmann's constant. In Eqs. (1) and (2), the so-called weak-coupling approximation, $N(0)V \ll 1$, is assumed. The gap Δ first decreases slowly with increasing T, but rapidly approaches to zero near T_0, because thermally excited electrons block possible pair states. The transition temperature T_0 is generally very low, less than 10 K for all simple metals, and does not exceed 25 K for any alloy. This fact is explained by the weakness of the attractive interaction.

The BCS theory has succeeded to a great extent in explaining various superconducting phenomena. However, some superconductors have been found to show a slight deviation from the original BCS theory. In order to explain the deviation, more realistic models have been constructed. Nevertheless, the main idea of the BCS theory, the pair formation and the energy gap appearance in the excitation spectrum of electronic state, still holds its validity.[8]

The superconducting property of Tc has been studied by many workers.[9~16] In these works, metallic ^{99}Tc has been used, because gram quantities of ^{99}Tc are available by separating fission products and the half-life is long enough. Of the various experiments, we refer to the experimental results of Trainor and Brodsky,[13] in which the heat capacity of Tc has been measured between 3 and 15 K. According to their results, the main superconducting parameter of Tc are as follows: $T_0=$ 7.86 K, the Debye temperature $\theta_D=454$ K, the magnetic critical field in the limit of 0 K is 1331 ± 10 Oe. They estimated the electron-phonon enhancement factor Λ and $N(0)$ to be 0.65 and 1.10 eV^{-1} atom^{-1}, respectively. The factor Λ, introduced by McMillan[17] to estimate the electron-phonon coupling intensity, approximately corresponds to $N(0)V$ in the BCS theory. The characteristic point in Tc is its large $N(0)$. For usual metals, $N(0)$ is a few tenth eV^{-1} atom^{-1}, but for Tc it is several times larger. This means that the *d* band of Tc is very narrow and *d* electron has a tendency to be localized around the ionic core.

Another important parameter, Δ was estimated by Sekula *et al.*[11] According to their result, $2\Delta/k_B T_0=3.54$, which is almost equal to the value calculated from Eqs. (1) and (2), 3.53. Therefore, Tc seems to be a weak-coupling superconductor, which is well explained by the BCS theory. However, the comparatively large $N(0)$ and Λ (for usual weak-coupling superconductors, Λ is around $0.3\sim0.6$) mean that Tc is not a simple weak-superconductor. Since *d* electrons tend to be localized around the ionic core, they give a strong Coulomb repulsion to each other, resulting in the reduction of the attractive force, $N(0)V$ or Λ. Consequently, the effective attractive interaction for pair formation becomes comparably weak.

As discussed above, in the superconducting state the conduction electrons have a tendency to form pairs mediated by the electron-phonon coupling. By this pair formation, it is expected that the electron density around the ionic core increases slightly. This localization of conduction electrons (4*d* electrons in this case) may cause a change in electronic state of Tc atom in the superconducting state. When compared with Tc_2S_7-metallic Tc pair,[7] the superconducting state is rather like the chemical state Tc_2S_7, where 4*d* electrons of Tc atom is more localized than in metallic Tc. However, the degree of 4*d* localization should be much smaller than that in Tc_2S_7, because the corresponding change in the atomic potential is very small. The difference in the atomic potentials between normal and superconducting states can be estimated by the gap energy Δ, which can be evaluated by $1.77\ k_B T_0\simeq1.2$ meV. On the other hand, between metallic Tc and Tc_2S_7, the difference is estimated to be a few eV, 10^3 times greater than Δ. If the change in the electron density at the nucleus is of the same order of the change in the atomic potential, the possible change in λ_{Tc} at the normal to superconducting transition is $\sim 10^{-7}$.

According to our experiment,[6] $\Delta\lambda/\lambda_{Tc}$ is zero within the experimental accuracy, 0.5×10^{-4}. Above consideration supports this result, but is inconsistent with the previous experiments, by Byers and Stump[2] with ^{99m}Tc and by Olin and Bainbridge[3] with ^{90m}Nb. They implied that the superconductivity has some effect on the core electrons and the resulting rearrangement of the atomic electrons brings about the observable change in the decay constant. According to the BCS theory, however, the superconducting effect on the rearrangement of the atomic electron system can not be so large. The above consideration suggests that the magnitude of the atomic-electron rearrangement due to the superconducting effect is less than 10^{-3} of that due to the chemical effect. In addition, there have been no evidences of other interaction to cause the superconductivity except the Cooper-pair formation. Consequently, we believe that the results found in the previous two experimental works are difficult to give a reasonable explanation, and that observation of $\Delta\lambda/\lambda$ due to the superconductnig effect is not technically possible at the present stage.

ACKNOWLEDGMENTS

The authors express their thanks to Dr. T. Mukoyama for valuable discussions.

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