The Latest Inspection of the Tc for the K1 model Superconductor

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Abstract :
As I mentioned in the latest bulletin of N.I.T, it is necessary to inspect the superconducting transition temperature (Tc) of K1 model sintered conductors because of its significant potential behaviour. One of the way to check it known for well is to measure the temperature dependence of the sudden drop resistivity. However, it will be hard to look at its own resistivity in the actual experiments as far as I know, and so the most of the informations about these attractive properties are supposed to calculate after the finished experiments. Therefore, if I can look them right in the middle of the visible experiments, I will be able to have much of the confidence in search of the Tc in this case. In this study, the way I look the dropping voltage instead of the dropping resistivity is considered and the Tc of K1 model sintered conductors are examined from the different points of view.

I. Introduction

First of all, the K1 model sintetered conductors were produced on July the 20th in 1997[1] and nowadays after much of three years, I can see the Meissner effect signal still more.
In my view, the Tc of K1 model has been reported three separate times in '97, '98 & '99 respectivery and the results in those days were only just the possibility of high (Tc) at first, (−) 136 ≦ Tc (℃) ≦ (−) 134 at second and approximately minus one hundred degrees centigrade at third. Contrary to general belief, they are not identical results one another. Why?, I can't see exactly now, but there are some doubts about the different outcome of this Tc investigation. As a matter of fact, I have some doubts whether the Tc on this sintetered conductors doesn't vary with the time passed. Including this doubt, I will make the investigation of the Tc in the peculiar manner once more.

II—A. Sample of the Superconductor

The sample of the superconductor is the Y based copper oxides ceramic materials and is keeping safely. Though it was produced much of three years ago, I can still look the Meissner effect signal at the low temperature environment with liquid nitrogeneven in this day. This is the present situation of the sample which I wish to examine this time, When I explain the way of how to examine the Tc, the first thing to do is to introduce the present situation of the sample. That is to say, the sample exists in the desiccator as few pieces of K1 model superconductors now. According to the measuring instrument, the measured resistance of the sample was at the most 100 【Ω/cm】, or about 40 【Ω/cm】 on average and the minimum one was about 15 【Ω/cm】 at the room temperature 27 (℃). Anyway, each of the values are already very small in comparison with the resistance of the raw materials because that the sample was the essential insulator before the sintering treatment. This is first significant fact on the change in quality of ceramic materials. Just to make sure that the measuring instrument indicates the correct values, as the standards, I used the resistor elements on the market. And, as a result of investigating many data, the measuring instrument indicates the correct values of the resistance.

II—B. Attaching the Conducting Wire

When the experiments will be carried out as planned, we usually need to attach the conducting wire on the sample. And it is needed for this experiments too, but we must be attentive to the attaching on the ceramic sample in particular. On this matter, J.W.Ekin of National Institute of Standards and Technology in USA reports some useful descriptions in his paper[2] and the applicable contents are as follows; The simplest method for attaching voltage leads to superconductors or noncritical connections (which do not require very low resistivity contacts) is to directly solder the lead wires to the superconductor with indium or indium-alloy solder. Indium-based solders are preferred because they have a melting temperature typically in the range 120(℃) to 160(℃), which is significantly lower than standard eutectic Pb-Sn solder (183 ℃), The lower melting temperature does not cause loss of oxygen or alter the anneal state of most high-Tc superconductors, as would be the case for Pb-Sn solders. Indium-based solders generally wet either bare or silver-sheathed high-Tc materials. Pure indium is quite soft, however, so an indium alloy such as eutectic In-48%Sn (melting temperature of 118 ℃) or eutectic In-3%Ag (melting temperature of 143 ℃) is preferred to obtain a strong contact, as well as lower the solder melting temperature. The best method for getting the solder to directly wet the surface of bare (non-silver sheathed) superconducting materials is to use an ultrasonic soldering iron, without any solder flux. Solder flux is death for most sintered high-Tc superconductors; the flux wicks into the superconductor along grain boundaries and deteriorates the grain boundaries and the transport properties of the superconductor. An ultrasonic soldering iron for high-Tc materials should be operated at a very low ultrasonic power and at a temperature less than 20 (℃) to 50 (℃) above the melting temperature of the solder, the higher temperature differential being used for large mass samples. For ultrasonic soldering to work well, the sample needs to be placed on a mechanically rigid surface. A drop of molten solder is applied to the sample with the vibrating solder tip; the vibration of the tip locally fractures tiny particles from the brittle superconductor's surface, exposing a fresh surface under the molten solder drop, which readily bonds to the indium. (Incidentally, ultrasonic soldering does not work at all on copper-lead wires or other ductile wire materials. In this case, solder flux is needed to chemically etch the oxide layer off the material and achieve solder wetting). For fragile superconductor samples, it is possible to patiently scratch the superconductor surface under a drop of molten indium-based solder until the solder eventually wets the surface (again without any solder flux). Not using an ultrasonic soldering iron lowers the likelihood of completely fracturing the superconductor sample. Silver paint, silver paste, or silver-based epoxy can also be used to attach voltage taps. Silver-paint and paste, however, are mechanically much weaker than solder, but for some delicate applications they are best. For silver-sheathed samples, the usual soldering technique works well, using a standard flux such as ZnCl. Again, solder having a low melting temperature, such as one of those recommended above, is best in order to keep from altering the anneal state of the superconductor. Considering the circumstances mentioned above, I would like to introduce the method for attaching voltage leads which I put into the practice of the experiments here. At first, the pure indium was used as based solders and was quite soft indeed, but it was possible to put the thin copper wire into contact with the ceramic samples. However, taking care not to break the brittle superconductor samples, I had to make the groove to fill with the thin copper wire leads (ϕ0.17 mm). And after grinding the surface of the wire to rub off the rust, I put the copper wire into the groove ofwidth less than or equal to 0.17 (mm). And then, the groove filled with the wire was covered with the pure indium to make the voltage taps and to obtain the strong contacts. In my view, making the groove was enough effective to obtain the strong contacts just as I mentioned above, but was not so much of troublesome if the simple tools such as sharp knife and thin screwdriver were prepared. However, as the strength of the contacts will have serious effect on the contact resistance at the voltage taps, the obtainning the strong contacts must be significant work in this research.

II—C. The Contact Resistance

To avoid the contact resistance has been concidered in this field of the resistance measurements. The contact resistance is usually very small, but is not small in comparison with zero resistance at the superconductive state of the samples. The definition of the contact resistivity and practical values are reported by Ekin[3] again as follows. Contact resistivity is expressed in terms of a specific contact resistivity $\rho c \equiv RA$, Where R is the contact resistance and A is the contact area. This gives a quantitative measure of interface quality that is independent of the contact area. There is no really good substitute for a good contact in high-current-density applications. The ρc values for magnet applications, as well as for the measurement of critical current, must be less than $\sim 10^{-4}$ to 10^{-5} Ω-cm^2 to prevent unacceptable heat and voltage generation at the current connections. Sometimes for critical-current measurement, pulsed current methods can be used to minimize heating, but then high frequency harmonics of the transport current can significantly affect the results. For thin-film package interconnections, on the other hand, nominal ρc values in the 10^{-8} Ω-cm^2 range are needed. For on-chip interconnections, low contact voltage requirements necessitate ρc in the 10^{-10} Ω-cm^2 range. Finally, for superconductor/normal-metal interfaces in josephson-junction applications, ρc values must typically be in the 10^{-11} Ω-cm^2 range, or lower. Therefore, the contact resistance is usually very small, but it have serious effect on the resistance of the samples which are at the state of superconductivity or closely related to it. Furthermore, the contact resistance is explained in Japanese dictionary of physics and chemistry[4] too, that is, the contact resistance is dependent on the shape of microscopic contact area, the cross section, oxide coatedfilm, and the condition of the adsorptive gas, but, to all appearances, is dependent on the pressure, the intensity of the electric current, and the career, etc . When the electric current increase, the contact resistance has the tendency to decrease. Now getting back to this text, I am considering whether to present the contact resistance at the experiments of Tc detection. This means that the contact resistance is negligiable quantity in comparison with the resistance of the samples (see II-A). If it is acceptable to the case of this experiments, I can introduce the requirements of the Tc detection, as follows;

(1) To put the samples into the direct-current circuit as the elements of resistance,

(2) To send the constant current into the circuit (It was kept at 0.13 【A】),

(3) To make sure the resistance at the room temperature.

As above mentioned, though I took no account of the contact resistance, it isn't impossible to measure the contact resistance, for example, Ekin says about it in his reports[2] as follows; The four-terminal measurement technique is typically used for measuring ρc of superconductor contacts. Current is injected into the superconductor through one contact pad and extracted from another. Two lead wires are attached to the current pad to be measured, one for introducing current, the other for detecting voltage at the surface of the pad. Another voltage tap is attached directly to the superconductor, as close as practical to the current pad (but not touching it). Below Tc where the base superconductor material has zero resistance, the contact resistance is just the voltage measured between these two voltage taps, divided by the current through the contact. Sometimes the resistance of the normal-metal pad affects the result, but usually this is small in comparison with the contact resistance. Above Tc, the measured value of ρc must be corrected for the resistance of the normal superconductor material between the contact pad voltage tap (marked 1) and the second voltage tap 2 by measuring the resistivity per unit length of the superconductor. This is done using another voltage tap 3 attached to the superconductor. Below Tc, however, where the sample is superconducting, no correction is needed. Accuracy of the ρc measurement is typically about $\pm 5\%$ to $\pm 10\%$. Generally it is a good idea to measure a series of contacts having different surface areas to ensure that spreading resistance in the contact pad is not affecting the result. Spreading resistance can be a problem when current is injected at only one point on the contactpad, and then must spread out throuh the thin normal metal contact pad to cover the entire contact area. This is quite common, especially with the small wires typically used in wire bonding. To ensure that this does not occur, the contact area is typically reduced or the contact pad thickness is increased until ρc no longer changes. In the limit of small contact areas, the sheet resistance of the contact pad does not affect the observed ρc. Note that the measured values are the voltage or the current, are not the resistance. This means that the contact resistance was the values which was calculated using the voltage and the current measured values. That is, the contact resistance was not obtained directly related to the measuring. So what I suggest is to observe the voltage substitute for the behaviour of the resistance to the current. If the suggestion is acceptable in this paper, the voltage in the direction of negative is supposed to observe at the constant curret (0.13 【A】). Even granting that this is an idea, it is significant work to make the current connections with the ceramic samples. On this subject of the methods, Ekin[2] says further; In fabricating contacts to high-Tc superconductors there are two main ploblems: (1) the superconductor surface degrades from exposure to air and other processing gases or liquids, and (2) the contact material itself can chemically degrade the superconductor surface and form a barrier layer at the contact interface. It is instructive to look at some of the early contact failures. These can be arranged in the upper part of his table[2]. Working down the list, we see that common Pb-Sn solder does not form a bond with YBCO. Silver paint adheres, but has a high interface resistivity. Indium, even when applied to a freshly exposed superconductor surface under molten solder, produces contacts with ρc not nearly low enough for practical applications. Sputter etching the superconductor surface in a vacuum and immediately depositing Cu or Au/Cr (a common semiconductor-contact material) without breaking vacuum produces no significant improvement. The problem is that common contact materials, while they may work well for normal-metal conductors, are not chemically suitable for making high-quality contacts to the oxide superconductors. Only one generic method has been found for solving these problems; it consists of three basic processing steps: (1) Clean the superconductor surface. (2) Use a noble metal for the contact material. (3) Oxygen anneal the noble metal/superconductor interface. The essential ingredient is the use of a noble metal as the contact material, because of the low affinity of these materials for oxygen. The third step (oxygen annealing) may be omitted if the surface preparation in the first step is good. [Generally, in making contacts, these fabrication steps performed sequentially as separate steps, but in the case of high-temperature coprocessing techniques, they occur simultaneously, although it's still essentially the same method.] Thus far, a generic contact method for the oxide superconductors involving a material system other than the noble metals has not been found. Typical results for contacts formed using the above method with unannealed silver and gold are shown in the lower part of the table. The difference in performance compared with the nonnoble-metal contacts in the upper part of table is striking; ρc is reduced by more than four orders of magnitude to the 10^{-6} Ω-cm^2 range. Oxygen annealing the contact interface after or during fabrication reduces ρc by another four orders of magnitude to the $<10^{-10}$ Ω-cm^2 range for a total reduction in ρc of over eight orders of magnitude compared with indium solder connections; Obtaining contact resistivities in this range is important for avoiding heating and high contact voltages, especially for applications requiring high contact current densities (both bulk and thin-film). The lowest contact resistivities obtained so far have reached the 10^{-10} to 10^{-12} Ω-cm^2 range using this generic contact method with either coprocessing techniques[4][5] or ultra-high-vacuum surface-preparation techniques[6][7]. Therefore, according to the Ekin's report, the contact resistance is very small and is negligible quantity at the current connections too. Thus, when I conduct the experiments of the Tc detection, the resistance of the superconductor samples may be the zero resistance at the state of superconductivity, but the resistance of the measuring circuit is not the zero because the contact resistance and the resistance of the wire leads are left at least. Fig. 1 shows the superconducting character of the V and T curves for indium-solder contacts with time passed. Where, the voltage is negative to the current and, note that this voltage is supposed to be show the behavior of the superconducting resistance. Here, in the time passed range of 13.3(sec) from 0.0 (sec). I checked the position where the resistance of the sample is marked at the ordinate. The marked (S) is the superconducting sample, the marked (2), (3), (4) are the resistive elements of 10, 20 33 【Ω】 on the market respectively, and the marked (S) is again checked just before the cooling with the liquid nitrogen. Therefore, it can safely be said that the resistance of the sample is in the range of 10< S 【Ω】 < 20 at the room temperature. In fact, the measured value of (S) was about 15 【Ω】 with the another digital tester. After the checking on these elements, the superconducting sample, that is, (S) was cooled by the liquid nitrogen all along

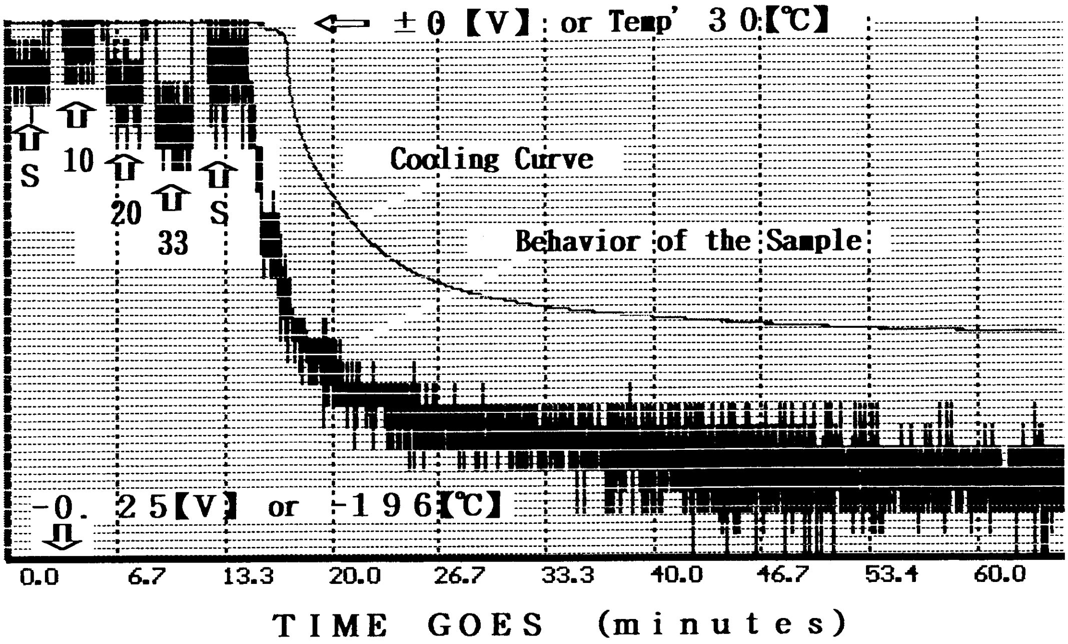

Fig. 1, The superconducting character of the K1 model sintered conductors with the cooling. Negative voltage to the constant current (0.13 [A]) shows the behaviour of the superconducting resistance and it shows the first sign of zero resistance begins to appear after about 20 minutes from the cooling started. The temperature at the time was about (−) 97 ℃. (Continued on the Fig. 2)

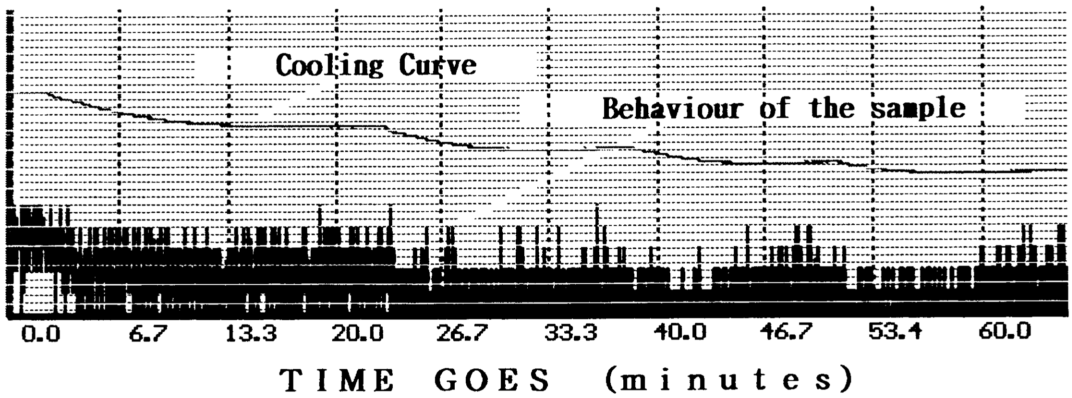

Fig. 2, The resistance of K1 model completely settles down to the range of zero resistance after about 50 minutes from the cooling started and the temperature at that time was about(−) 120 ℃.

the cooling curve (T). After about 1597 (seconds) from the cooling started, we can find the first sudden drop in the behavior of (S). This may be also first signs that the superconductivity is beginning. If it is right in the observation, the temperature at that time is significant as a matter of course. As the data in this observation are taken once per second, it is possible to find out the applicable temperature from the large amount of digital data. According to the data I have hare, the 2543th datum corresponds to it and was (−) 96.87 (℃). After about 3010(seconds) from the cooling started, we can find that the behavior of (S) completely settles down in the low resistance. As the 1413th datum in the Fig. 2 corresponds to this, the Tc of the sample can safely be said that it is higher than (−) 119.69 (℃). Consequently, the Tc of this sample is in the range of (−) 120 < Tc(℃)<(−) 97 even if I made a rather low estimate. There is another datum that the temperature (−) 97 (℃) is considered as the Tc. That is, Fig. 3 plotting the correlation between the behaviour of resistance and the cooling temperature says that the sample gets the superconductivity to some extent at the cooling temperature (−) 96.55 (℃) (look carefully at the point of an arrow).

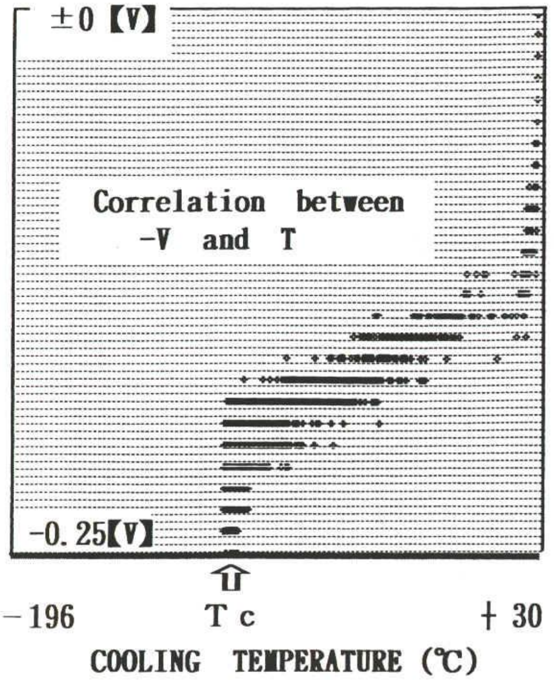

Fig. 3, Correlation between negative voltage and the cooling temperature. This figure hinted at the possibility of the Tc detection with the zero resistance.

Further, Fig. 4 is a photograph of the actual state on the observations and is enough to accept that the samples still send the Meissner effect signal even if it is separated into small pieces of the ceramic superconductors.

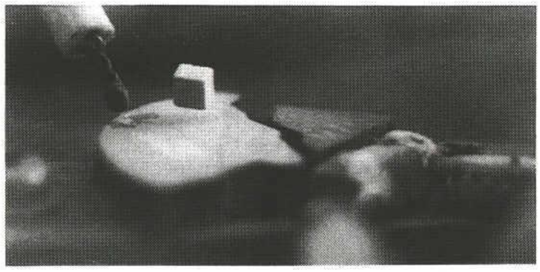

Fig. 4, Even now, the K1 model works as well as the original one of three years ago, and can still send the Meissner effect signal even if it is separated into small pieces of the brittle ceramics.

III. Conclusions

To tell the truth, I've been specially wondering if the K1 type HTS will work as well as the last HTS because of its excellent superconductivity I've never seen. Among of all others, the higher Tc has attracted considerable attention since the latest reports. Therefore, I examined the Tc of the HTS with the different method from the last one, once more. As the results that I have examined so far, I can safely be said that are:

(1) The K1 type HTS can still send the Meissner effect signal even if it is separated into small pieces of the brittle ceramics,

(2) The K1 type HTS can, still now, work as well as the original one, of three years ago,

(3) About (−)97(℃)was detected as the Tc.

In conclusion, I wish the Tc examined for this superconductor were exactly and were useful as the data, but it is so high that I will not be able to put the much of confidence because the world's highest Tc now is about (−)103(℃)[8] as far as I know.

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