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Studies of Magnetic Properties of High-T_c Copper-Oxide Superconductor Systems by μSR Methods

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Studies of magnetic properties of high-T_c superconductor systems by using $\mu^{\pm}$SR methods are reviewed briefly. μ^+SR has been very powerful to detect a static 3D-antiferromagnetic ordering in the insulating phase and has been used to study how the antiferromagnetism will be modified by changing the content of oxygen atoms or doping elements. The magnetic phase diagrams of various high-T_c copper-oxide superconductor systems have been obtained by μ^+SR. In the $YBa_2Cu_3O_x$ system, the coexistence of superconductivity and some sort of magnetic ordering at low temperatures has been discussed in terms of the oxygen-ordering and the mixture of superconducting and insulating micrograins. Non-observation of magnetism of electronic origin by μ^+SR, implies that some theories of high-T_c superconductivity, such as anyon mechanism, is unlikely. μ^-SR methods are expected to reveal different aspects of high-T_c oxide-superconductors from μ^+SR, since μ^-, trapped by nuclei in the material, forms a muonic atom. Microscopic studies of the electronic state at oxygen sites in high-T_c oxide-superconductors or 3d-transition element oxides by μ^-SR are also discussed.

KEYWORDS: μSR, high-T_c oxide-superconductors, anyon, antiferromagnetism, magnetic phase diagram

All the experimental and theoretical methods which have been developed for studies of solid state physics have been used in order to study a mechanism of high-T_c superconductivity. Muon Spin Rotation or Relaxation (μSR) methods have made important contributions to studies of the magnetic properties and to measurements of the superconducting magnetic penetration depth of high-T_c superconductors. Here, the studies of high-T_c superconductor systems by using positive (μ^+) and negative (μ^-) muons are briefly described.

§1. Studies of High-T_c Superconductor Systems by Using Positive Muons

1.1 *Antiferromagnetism of high-T_c superconductor systems probed by μ^+SR*

In the first high-T_c superconductor, $La_{2-x}A_xCuO_{4-\delta}$ (A=Sr or Ba), since the mother material, $La_2CuO_{4-\delta}$, was found to be an antiferromagnetic insulator from the bulk magnetic susceptibility measurements, the importance of magnetism has been proposed in order to explain the high-T_c superconductivity.[1] However, in a $YBa_2Cu_3O_x$ system whose superconducting transition temperature exceeded liquid nitrogen temperature for the first time, the magnetic properties were not clear from χ measurements. NMR experiments and neutron experiments were not able to find antiferromagnetic ordering in the insulating phase of $YBa_2Cu_3O_x$. Therefore, in order to consider a mechanism of high-T_c superconductivity, it was an important point to know whether the magnetic properties of $YBa_2Cu_3O_x$ are similar to those of $La_{2-x}A_xCuO_{4-\delta}$ (A=Sr or Ba) or not.

Even at the early stage of sample preparation where several impurity phases are contained in the sample, μ^+SR methods are very useful to probe magnetism of a main phase in the sample, as explained in the followings. (1) Polarized μ^+ is a purely magnetic probe (μ^+ spin is 1/2). (2) The total amplitude of μ^+SR signal is self-calibrated. (3) Even if the sample is not single-phased, μ^+SR can be considered to be a magnetometer which is selectively sensitive to magnetism of the main phase in the sample, since the signal amplitudes from the impurity phases are proportional only to their amount in the sample. Therefore, μ^+SR was applied to studies of magnetism of $YBa_2Cu_3O_x$ by changing the oxygen content systematically. Then, μ^+SR succeeded in finding 3D-antiferromagnetic ordering with high Neel temperature in the insulating phase of $YBa_2Cu_3O_x$[2] and have revealed that the $YBa_2Cu_3O_x$ system has the similar magnetic phase diagram[3-5] against oxygen content to that of $La_{2-x}A_xCuO_{4-\delta}$ (A=Sr or Ba) against doping content. These results by μ^+SR were later confirmed by neutron scattering experiments[24] and NMR measurements.[25] Thus, μ^+SR has been very powerful to study gross features of magnetic properties in high-T_c copper-oxide superconductor systems. The magnetic properties of various copper-oxide high-T_c superconductor systems, such as $YBa_2Cu_3O_x$,[2-5] $HoBa_2Cu_3O_x$,[6-8] $GdBa_2Cu_3O_x$,[9,10] $La_{2-x}Sr_xCuO_{4-\delta}$,[11-13] $Bi_2Sr_2Y_{1-x}Ca_xCu_2O_y$,[14-17] $Bi_2(Sr_{1-x}La_x)_2CuO_y$,[18] $La_2CaCu_2O_x$,[19] $H_xYBa_2Cu_3O_y$,[20] $Pr_{1-x}Y_xBa_2Cu_3O_7$,[21,22] $(Ln_{1-x}Ce_x)_2CuO_{4-y}$ (Ln=Pr, Nd, Sm),[23] have been studied by μ^+SR.

Although μ^+SR has been powerful to detect 3D-antiferromagnetic ordering and make magnetic phase diagrams in high-T_c copper-oxide superconductor systems, it could detect neither 2D-short-range ordering which has been observed by neutron scattering experiments[26,27] above T_N in the insulating phase, nor magnetism of electronic origin, such as magnetic fluctuations, which have been observed by NMR[28] in the normal state of the superconducting phase. Probably, the time scale of magnetic fluctuations to be observed in high-T_c oxide-superconductors is not relevant for μ^+SR. Therefore, the μ^+SR studies of high-T_c superconductor systems have been concentrated on how the 3D-antiferromagnetic static ordering will be modified by the presence of carriers. In hole-carrier high-

T_c superconductors, T_N decreases rapidly by introducing holes; T_N vanishes by only 2% doping. On the other hand, in electron-carrier high-T_c superconductors, T_N stays almost constant even up to ~10%.[23] These are interpreted as follows: in case of hole-doping, holes are introduced into oxygen sites in CuO_2 planes and super-exchange interactions between copper moments are much influenced, while in case of electron-doping carriers bring about a conversion of Cu^{++} to Cu^+ and just magnetic dilution occurs.[23,29]

Neutron scattering experiments have characterized the antiferromagnetism of $YBa_2Cu_3O_6$ or $La_2CuO_{4-\delta}$ as a quasi-2D spin 1/2 Heisenberg antiferromagnet with a weak XY-anisotropy and interplanar coupling.[27,30] Since the temperature dependences of the internal magnetic fields at μ^+ sites, $B_\mu(T)$, can be measured accurately, we can study how the sublattice magnetization will change with temperture. In Fig. 1 the $B_\mu(T)$ is shown for $La_2CuO_{4-\delta}$. A rather rapid decrease of $B_\mu(T)$ at low temperatures will show a quasi-2D character of this spin system. The detailed discussions have not been done. The main contribution to $B_\mu(T)$ is magnetic dipolar fields, B_{dip}, which is very sensitive to a rotation or canting of magnetic moments. Therefore, a peculiar temperature dependence of $B_\mu(T)$ have ben observed in $YBa_2Cu_3O_6$[3,31] or $Bi_2Sr_2YCu_2O_y$,[17] $Nd_2CuO_{4-\delta}$[23] or $Pr_2CuO_{4-\delta}$; these also have not been discussed well.

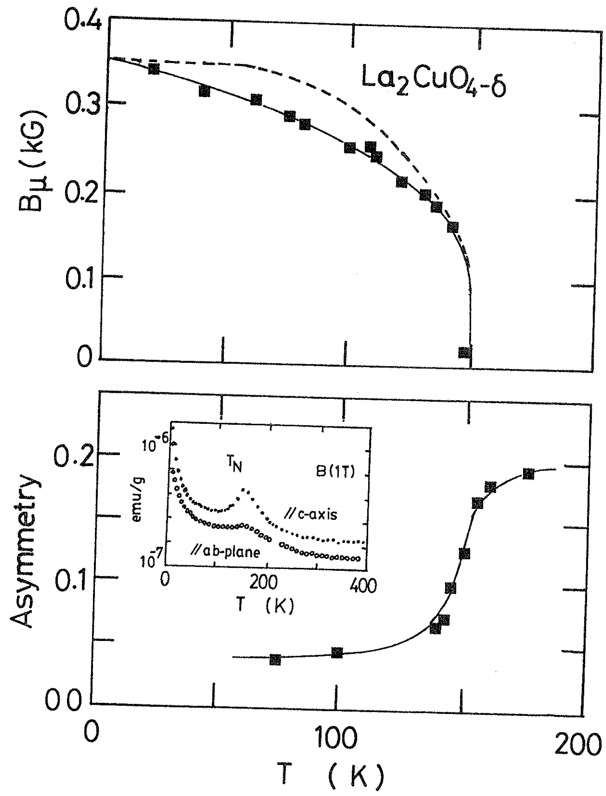


Fig. 1. (a) The temperature dependence of $B_\mu(T)$ in the single crystal $La_2CuO_{4-\delta}$ (T_N=153 K) is shown. The $B_\mu(T)$ decreases with increasing temperature faster than the molecular field calculation (dotted line). (b) The results of TF-μ^+SR are shown: the sharp decrease of the μ^+ spin precession amplitude guaratees a uniform distribution of oxygens in the sample. The temperature dependence of χ is also shown.

1.2 *Magnetic phase diagram of $YBa_2Cu_3O_x$*

In the critical region of carrier content near metal-insulator transision, the coexistence of superconductivity and spin-glass-like magnetic ordering or antiferromagnetism has been reported in $YBa_2Cu_3O_x$[3,5] and $La_{2-x}A_xCuO_{4-\delta}$ (A=Sr or Ba).[12,13] In copper-oxide high-T_c superconductors, a superconducting coherence length is very short, ~20 Å. Therefore, if superconducting and antiferromagnetic grains of few tens of Å are mixed up in the sample, it is difficult to determine whether the observed physical properties are intrinsic one or due to mixtures of diffrent phases.

In $YBa_2Cu_3O_x$, chemical and physical properties, such as behavior of oxygen atoms in the crystal, have been most elaborately studied. Let us think about the coexistence of superconductivity and magnetism in $YBa_2Cu_3O_x$ system. In Fig. 2 are shown the magnetic phase diagrams of $YBa_2Cu_3O_x$ which have been obtained by μ^+SR[3-5] and neutron scattering experiments[30,32,33] for samples of diffrent heat treatment. Influences of oxygen-ordering on physical properties can be seen clearly in this figure. Brewer *et al.* performed μ^+SR experiments[5] on two sets of $YBa_2Cu_3O_x$ samples; the oxygen contents of one set of samples are varied by quenching them into liquid nitrogen from appropriate oxygen atmosphere at high temperatures and those of the other set by annealing them in appropriate oxygen atmosphere for ~24 hours. The T_N's stays almost constant up to x~6.2 for both sets. A rapid decrease of T_N can be seen at x=6.2~6.3 for annealed samples and at x=6.3~6.4 for quenched

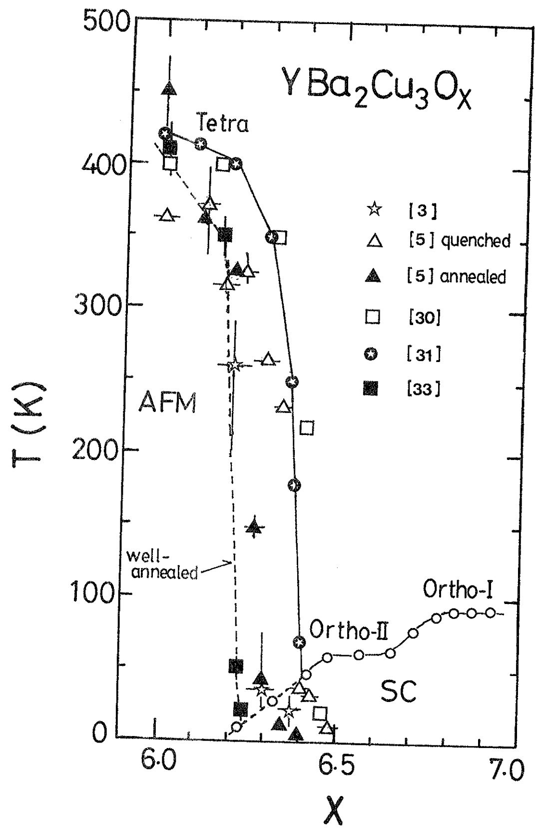


Fig. 2. Magnetic phase diagrams obtained by μ^+SR and neutron scattering experiments in the $YBa_2Cu_3O_x$ system are summarized. The references are shown in the figure.

samples. Nakazawa *et al.*[34] was able to stabilize the orthorhombic phase down to $x \sim 6.2$ by annealing $YBa_2Cu_3O_x$ in appropriate oxygen atmosphere for more than 50 hours. The dotted line shows T_N's of those samples from neutron experiments by Rebensky *et al.*[33] T_N shows a steplike decrease around $x \sim 6.2$. Their samples which show magnetic ordering at low temperatures are reported to exhibit superconductivity. The solid line show T_N's for quenched samples where no trace of superconductivity were observed. The neutron data by Rossat-Mignot *et al.*[30] and Tranquada *et al.*[19] are shown. In Fig. 2 it will be noticed that T_N's up to $x \sim 6.2$ do not depend on thermal treatment so much and that at $x=6.2 \sim 6.4$ T_N's are between the above mentioned two lines, depending on the thermal treatment. In some samples with $x=6.2 \sim 6.4$, coexistence of superconductivity and antiferromagnetism has been observed. In oxygen-ordered $YBa_2Cu_3O_{6.5}$ of Ortho-II phase, it is reported by Nishida *et al.*[35] that no magnetism of electronic origin can be observed by μ^+SR. These will be interpreted as follows: In $YBa_2Cu_3O_x$, oxygen atoms tend to line in CuO chains and this ordering has an important role to introduce carriers to CuO_2 planes. Therefore, in the intermediate region of $x=6.2 \sim 6.4$ the physical properties are sensitive to heat treatment. The coexistence of superconductivity and some kind of magnetic ordering at lowe temperatures can be explained in terms of mixture of superconducting and insulating micrograins. The μ^+SR results for the samples exhibiting both superconductivity and some static magnetic ordering are consistent with a picture of mixture of two different phases, if the size of micrograins is ~ 50 Å. The details should be refered to ref. 36).

1.3 *Possibility of anyons*

μ^+SR has not detected magnetism of electronic origin in the superconducting phase of $YBa_2Cu_3O_x$ ($x=7$, 6.5). This experimental fact supplies us an interesting by-product for the understanding of high-T_c superconductivity.[35,39] Halperin *et al.*[37] proposed that if the electronic state of high-T_c superconductor has a broken time-reversal symmetry, static magnetic fields of several tens of Gauss might be observed by μ^+SR under zero applied field, since implanted μ^+ repel holes in hole-carrier high-T_c superconductors and bring about charge unbalance around μ^+. The non-observation of magnetic fields of electronic origin by μ^+SR[3,35,39] implies that some theories of high-T_c superconductivity, such as anyon mechanism,[38] might be unlikely. The details are described as follows.

In Fig. 3 are shown the μ^+ spin relaxation function $G_z(t)$'s of $YBa_2Cu_3O_7$ in zero external field: Below 200 K they have the same shape and are well fitted by a static gaussian Kubo-Toyabe function with $\Delta=0.12 \pm 0.01$ μs^{-1}.[3] This value agrees with the results by Kiefl *et al.*[39] Above 200 K, they are narrowed due to μ^+ motion in the crystal and can be fitted by a dynamic Kubo-Toyabe function with the same Δ and the hopping frequency ν; the temperature dependence of ν is well represented by Arrhenius formula $\nu=\nu_0 \times \exp(-E_a/kT)$ with $\nu_0=2.3 \pm 1.5 \times 10^8$ and $E_a=1580 \pm 180$ K. This means

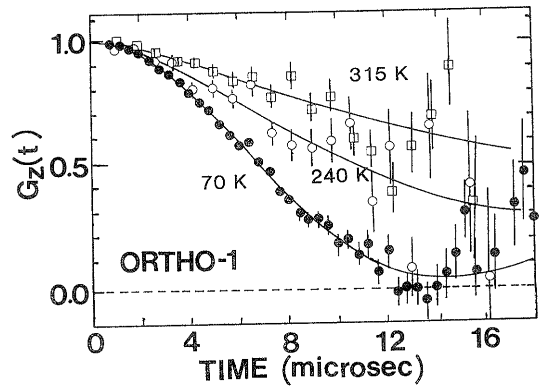


Fig. 3. The $G_z(t)$ of $YBa_2Cu_3O_{6.9}$ are shown. The $G_z(t)$ take the same shape below 200 K and only the data at 70 K is shown. The motional narrowing effects can be seen. They are fitted by a dynamic Kubo-Toyabe function with the same Δ below 200 K.

that both below and above T_c static magnetic fields distributed around zero with a standard deviation of 1.4 G have been probed by μ^+. In oxygen-ordered $YBa_2Cu_3O_{6.5}$ of Ortho-II phase, the same μ^+ spin relaxation function $G_z(t)$ as in $YBa_2Cu_3O_7$ has been observed and the same value of Δ has been obtained. In order to discuss the origin of static magnetic fields observed in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.5}$ quantitatively, it is necessary to determine the μ^+ sites in $YBa_2Cu_3O_x$. From the analysis of μ^+ hyperfine magnetic fields in antiferromagnetically ordered $YBa_2Cu_3O_6$ and $GdBa_2Cu_3O_7$, we were able to discuss the μ^+ sites.[35] Thus determined μ^+ sites are summarized as follows and they seem to be well described by ionic crystal picture: In 1-2-3 compounds the positive muons are repelled by cations Y^{3+}, Ba^{2+} and $Cu^{2+\text{ or }1+}$ and attracted by negative O^{2-}, make O-μ^+ bondings analogous to OH and the directions of the O-μ^+ bondings take as far as possible from cations Y^{3+}, Ba^{2+} and $Cu^{2+\text{ or }1+}$ with some modification by being attracted by neighboring negative O^{2-}. In Fig. 4 the candidates of μ^+ sites are shown schematically.[35] In $YBa_2Cu_3O_7$ where oxygen atoms in CuO chains are almost perfect, most of μ^+ make O-μ^+ bonding with oxygen atoms (O(1)) in Cu–O chains (a-sites in Fig. 4). When oxygen atoms become deficient in Cu–O chain, μ^+ seems to mainly stay near oxygen atoms (O(4)) in Ba–O layer (b-sites in Fig. 4), although a small portion of implanted μ^+ may stay near oxygen atoms O(2, 3) in CuO_2 plane (c-sites in Fig. 4). Several μSR groups[35,40,41,8] have proposed the possible μ^+ sites in 1-2-3 compound. At the present they do not agree with each other, but the above-mentioned sites are among their candidate sites. When we calculate the second moments of nuclear magnetic dipolar fields from Cu, Y and Ba nuclear magnetic moments at those proposed μ^+ sites, they almost coincide with the observed experimental value. Thus, the observed static magnetic fields probed by μ^+SR will be interpreted by nuclear magnetic dipolar fields from nuclear moments of Cu, Y and Ba in the order of 0.1 G.

§2. Studies of High-T_c Superconductor Systems by Using Negative Muons

Thus far, the studies by using μ^+ have been described.

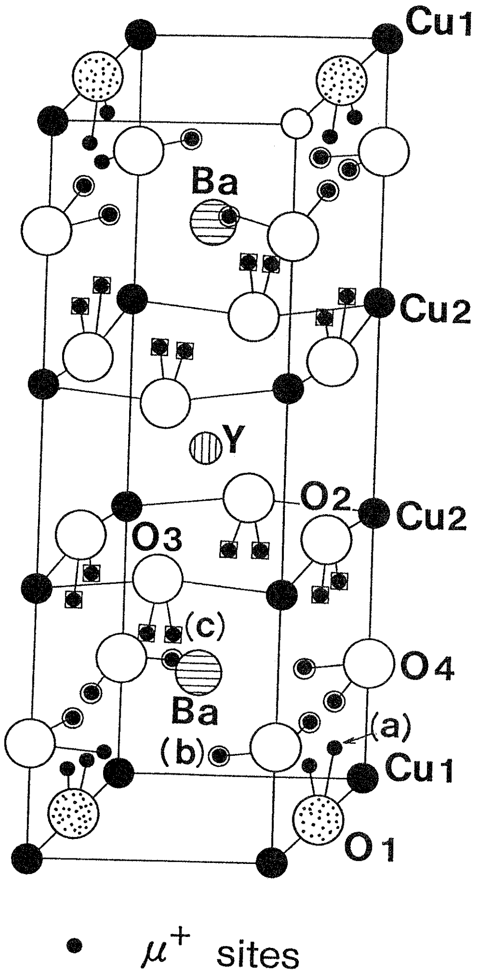


Fig. 4. A schematic diagram of μ^+ sites in $YBa_2Cu_3O_x$ is shown (ref. 35). It was obtained from a discussion about the obserbed internal magnetic fields at μ^+ sites in various magnetically ordered 1-2-3 compounds. In $YBa_2Cu_3O_6$ the b-sites are the main μ^+ sites; some μ^+ occupy c-sites. When oxygen atoms are present in the Cu1 plane, the a-sites are occupied. In $YBa_2Cu_3O_7$ the a-sites are considered to be the main occupied sites of μ^+.

Positive muons (μ^+) behaves like protons in the material and in oxides μ^+'s are considered to form O-μ^+ bonding analogous to O–H and to stay near oxygen atoms. μ^+SR can be compared to *proton resonance*. When negative muons (μ^-) are used for studies of oxide-superconductors, another feature will appear: μ^-, implanted into the material, is captured by an atomic nucleus, emitting muonic X-ray, it goes down to muon $1s_{1/2}$ orbit (the radius is about 1/200 smaller than that of electron bohr orbit) and a muonic atom is formed. A muonic atom is a quais-nucleus with spin 1/2 (in case of spin zero atomic nucleus) and a large magnetic moment. The initial polarization of μ^-spin decreases during the cascade, but still remains at $1s_{1/2}$ orbit, though the magnitude is reduced to 1/6. Thus, we can perform μSR experiment by using polarized negative muons. The μ^- in muonic atom has a probability to be absorbed by nucleus and has a mean lifetime which is different from that of a free μ^- in vacuum and depends on an atomic number, Z, of the captured nucleus (~ 1.8 μs for muonic oxygen and ~ 0.08 μs for muonic lead). Therefore, in high-T_c oxide-superconductors, μ^-SR is capable of identifying μ^-e decay electrons of muonic oxygen from those of muonic atoms of other heavy elements. Thus, μ^-SR can be compared to *impurity NMR*. Since a radius of muonic atom is very small, a muonic atom is equivalent to (Z-1)-nucleus for surrounding electrons; muonic oxygen is equivalent to nitrogen nuclei. In copper-oxide high-T_c superconductors, a muonic oxygen becomes an anomalous point in CuO_2 network and is expected to be a unique microscopic probe to give some new information concerning the electronic states at oxygen sites.

μ^-SR experiments have been performed[42-44] on several oxides, such as $La_2CuO_{4-\delta}$, $La_{2-x}Sr_xCuO_{4-\delta}$, $Nd_{2-x}Ce_x CuO_{4-\delta}$ (x=0.15), $YBa_2Cu_3O_x$, CuO, Cu_2, $LiTi_2O_4$, MnO, MgO. Since it takes much longer time for μ^-SR to accumulate data than μ^+SR, μ^-SR experiments have not been performed so widely as μ^+SR; only Japanese group has been involved in it.

The paramagnetic shifts, K_{μ^-}, of muonic oxygen (O_{μ^-}) have been measured in some oxides of 3d-transition elements. In Fig. 5[43] the K_{μ^-} are plotted against bulk magnetic susceptibility, χ. In copper oxides, K_{μ^-}'s are all positive and of the order of 10^{-3}. In $LiTi_2O_4$, K_{μ^-} has been measured as $8.4 \pm 3.3 \times 10^{-5}$, which is smaller by more than one order of magnitude than those of copper-oxides, though the χ are not so different among those materials. This will have relation with the picture from photoelectron spectroscopy experiments on transition element oxides; in oxide-insulators for transition elements at the latter part in the periodic table, the Cu 3d and O 2p levels are close and strongly hybridized each other and due to a charge transfer between Cu^{++} and O^{--}, a large paramagnetic shift might be expected in copper-oxides, while in oxide-insulators for those at the early part, O 2p level is situated at a deep position, compared with Cu 3d level and a small K_{μ^-} might be observed. The further systematic studies, including studies of temperature

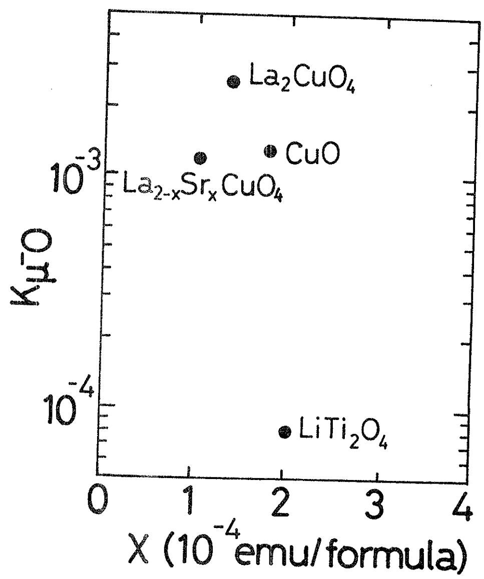


Fig. 5. The paramagnetic shifts K_{μ^-} of $O\mu^-$ at 300 K in various oxides are plotted against bulk magnetic susceptibilities χ at 300 K. The K_{μ^-} are all positive with a magnitude of $+10^{-3}$, while in $LiTi_2O_4$ K_{μ^-} is smaller than one order of magnitude.

dependences, are necessary. In the single crystal $La_{2-x}Sr_xCuO_{4-\delta}$, detailed measurements[42] of K_{μ^-}, such as temperature dependences and the crystal axis dependence, have been reported. Microscopic theoretical calculations are waited for.

The μ^-SR results in $YBa_2Cu_3O_x$ system[44] are very different from $La_{2-x}Sr_xCuO_{4-\delta}$ system.[42]

In $La_{2-x}Sr_xCuO_{4-\delta}$ ($x=0.14$) of the superconducting phase, μ^-SR signal has been successfuly observed with the $T_2\sim2.5\,\mu$s which is not so different from T_2 in $La_2CuO_{4-\delta}$ ($\sim1\,\mu$s) of insulating phase.

In the paramagnetic phase of insulating $YBa_2Cu_3O_6$ at 500 K and 550 K in 9.2 kG, the μ^- spin precessions were observed as shown in Fig. 6(a). The K_{μ^-} have been determined as being $4.6\pm1.9\times10^{-4}$ at 500 K and $8.7\pm1.7\times10^{-4}$ at 550 K. The T_2 was about 1.4 μs at both temperatures. The precession amplitude was about 2/3 of the full signal. The very fast relaxing component ($T_2=\sim150$ ns) can be seen in the beginning part of the μ^-SR spectra. They are from oxygens in CuO_2 planes and apical oxygens, although the site assignment has not been performed.

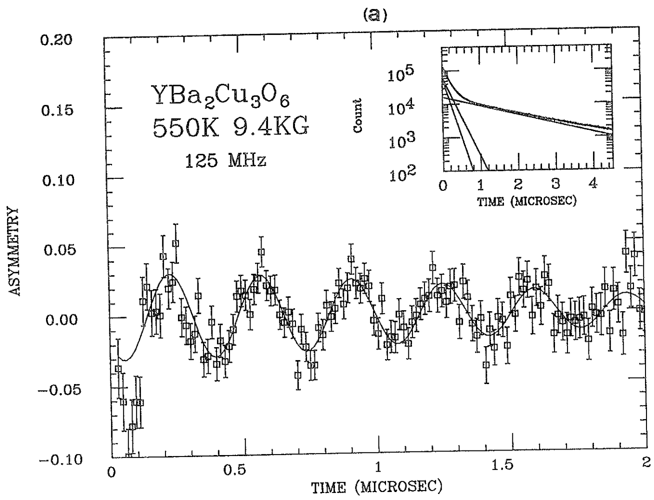
In $YBa_2Cu_3O_7$, Ortho-II $YBa_2Cu_3O_{6.5}$ and $GdBa_2Cu_3O_7$ where holes are present, the μ^-SR signal decays so fast that the K_{μ^-} could not be determined; the μ^-SR spectra of $YBa_2Cu_3O_7$ in 6.2 kG at 100 K is shown in Fig. 6(b). The T_2 is 100~200 ns, which is faster by nearly one order than T_2 in the insulating $YBa_2Cu_3O_6$. This is opposite to the case in $La_{2-x}Sr_xCuO_{4-\delta}$.

In the $YBa_2Cu_3O_x$ system, the difference of μ^-SR signals has been outstanding between in the superconducting phase ($x=7$, 6.5) and in the insulating phase ($x=6$); the μ^- spin relaxation time is much faster in the superconducting phase. This makes quite a contrast with that in doped high-T_c oxide-superconductors. The reason is not known.

§3. Summary and Conclusions

In the studies of high-T_c superconductor systems, μ^+SR have been very powerful in detecting static magnetic orderings and have succeeded in revealing a lot of 3D-antiferromagnetic orderings in their insulating phases. However, μ^+SR could detect neither 2D-short-range magnetic orderings observed in the insulating phase above T_N by neutron scattering experiments, nor magnetic fluctuations observed in the normal state of the superconducting phase by NMR. The absence of static magnetic fields of electronic origin probed by μ^+SR in the $YBa_2Cu_3O_7$ or $YBa_2Cu_3O_{6.5}$ indicated that some theories of superconductivity, such as anyon mechanism, are unlikely. Thus, μ^+SR studies of high-T_c superconductor systems have been concentrated on how the static 3D-antiferromagnetic ordering of the insulating phase will be modified by the presence of carriers. In the critical carrier concentration region, the coexistence of superconductivity and spin-glass-like magnetic ordering has been reported by μ^+SR experiments. This problem need more studies with special attentions to oxygen ordering or homogeneity of oxygens or doping elements in the sample. In the $YBa_2Cu_3O_x$ system, the effect of oxygen-ordering on magnetic properties has been shown in the magnetic phase diagram from μ^+SR and neutron scattering experiments. The coexistence of superconductivity and some sort of magnetic ordering at low temperatures in the critical region of $YBa_2Cu_3O_x$ system has been in terpreted in terms of the mixture of insulating and superconducting micrograins of the size ~50 Å.

In the μ^-SR studies on $YBa_2Cu_3O_x$ ($x=7$, 6.5 and 6), the μ^- spin relaxation time was found to be faster by almost one order of magnitude in $YBa_2Cu_3O_7$ or $YBa_2Cu_3O_{6.5}$ than in $YBa_2Cu_3O_6$. This makes a contrast with that in doped high-T_c superconductors, such as $La_{2-x}Sr_xCuO_{4-\delta}$ or $Nd_{2-x}Ce_xCuO_{4-\delta}$ ($x=0.15$), in which the μ^- spin relaxation time does not show any drastic change in superconducting and superconducting phases. At the present the reason is not known, but this may imply why the T_c of doped high-T_c oxide-superconductors are below 40 K and lower than stoichiometric compounds, such as $YBa_2Cu_3O_7$ or $Bi_2Sr_2CaCu_2O_y$. The $O\mu^-$ shift in $LiTi_2O_4$ was found to be smaller by one order of magnitude than those in various copper-oxides. A systematic studies of $O\mu^-$ shifts in 3d-transition oxides will be



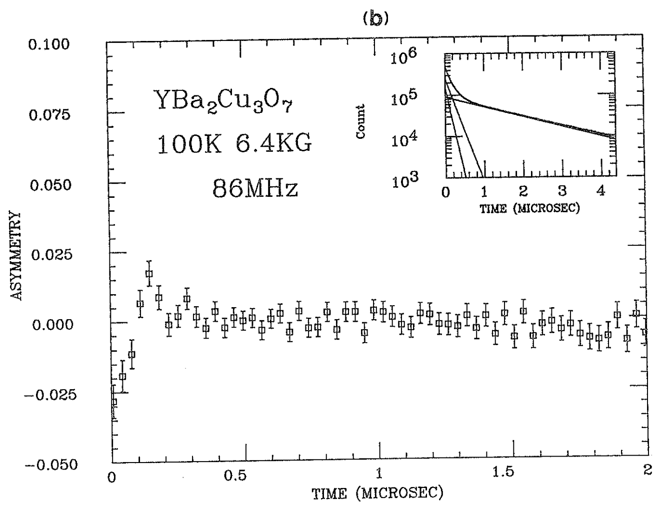


Fig. 6. (a) μ^-SR spectrum in $YBa_2Cu_3O_6$ at 550 K in 9.4 kG. In the insert figure, the components of μ^--e decay from Y, Ba, Cu and O. (b) μ^-SR spectrum in $YBa_2Cu_3O_7$ at 100 K in 6.4 kG.

interesting problems in order to understand the electronic states of oxygen sites in the oxides of 3d-transition elements.

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