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^{99}Ru (←^{99}Rh) as a TDPAC Probe in the Study of a High-T_c Superconductor

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A radiochemical procedure has been established to dope carrier-free ^{99}Rh in $YBa_2Cu_3O_{7-x}$. The time-differential perturbed-angular correlation of γ-rays emitted from the nuclear excited levels of the daughter nuclide ^{99}Ru in the superconducting and semiconducting samples with x ≃ 0.2 and 1.0, respectively, revealed the hyperfine electric quadrupole interaction for the former and the magnetic interaction in addition for the latter. The results have shown that ^{99}Ru is a useful hyperfine-interaction probe comparable to ^{57}Fe.

Various hyperfine-interaction techniques using unstable nuclei as probes have been applied to the study of high-T_c superconductors since the discovery in 1986. In Mössbauer absorption spectroscopy, which has been most frequently utilized,[1,2] introduction of a certain amount of probe nuclei into the matrix is inevitable, resulting in some degree of alteration of its bulk properties. However, in time-differential perturbed-angular correlation (TDPAC) of γ-rays,[3] as in Mössbauer emission spectroscopy,[4] the amount of probes necessary for measurement is so small that they can be regarded as infinitely diluted impurities having little effect on the bulk. Thus far, TDPAC nuclides ^{99}Mo → ^{99}Tc,[5] ^{111}In → ^{111}Cd,[6] ^{140}La → ^{140}Ce,[7,8] and ^{181}Hf → ^{181}Ta[8] have been used as probes in the study of high-T_c superconductors. In order to exploit the usefulness of the technique further, we have established a radiochemical procedure to dope ^{99}Rh in $YBa_2Cu_3O_{7-x}$ samples and measured the TDPAC of γ-rays emitted from its daughter nuclide ^{99}Ru (Fig. 1).[9]

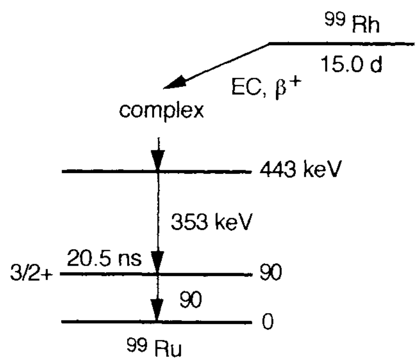

Fig. 1. Simplified decay scheme of ^{99}Rh (only nuclear energy levels and transitions relevant to the present work are shown).

The oxide, $YBa_2Cu_3O_{7-x}$, is orthorhombic and superconducting for 0 ≤ x ≤ 0.7, but is tetragonal and semiconducting for 0.7 ≤ x ≤ 1. There are two orthorhombic phases, ortho-I (0 ≤ x ≤ 0.15, T_c = 93 K) and ortho-II (0.35 ≤ x ≤ 0.55, T_c = 58 K). In both the orthorhombic and tetragonal structures, there are two distinctive sites for copper. The first site (Cu-1) is between two Ba layers, and forms one-dimensional Cu-O chains in the orthorhombic phases. The second site (Cu-2), between the Y and Ba layers, constitutes corrugated two-dimensional planes in both the orthorhombic and tetragonal phases. The planes form the superconduction layers in the orthorhombic phases.

About 80 mg of isotopically enriched (96.63 %) ^{99}Ru metal powder enveloped in Al foils was irradiated with 13-MeV protons available from the INS-SF cyclotron. The (p, n) reaction produces ^{99}Rh (half-life 15.0 days) from ^{99}Ru. The irradiated target was put in a KOH solution with a layer of CCl_4 at the bottom. Ruthenium metal was oxidized to RuO_4 by passing Cl_2 gas through the suspension and was extracted with CCl_4. Carrier-free $^{99}Rh^{3+}$ remaining in the aqueous phase was purified by coprecipitation with iron (III) hydroxide and by anion exchange.[10]

As the first step of introducing carrier-free $^{99}Rh^{3+}$ ions homogeneously in $YBa_2Cu_3O_{7-x}$, we adopted their adsorption on one of the starting materials from an aqueous solution. Radioactive tracer experiments were performed to determine the pH dependence of adsorption of $^{99}Rh^{3+}$ ions on Y_2O_3 and CuO powders. The ions showed high adsorption on CuO in the alkaline region, as shown in Fig. 2. Consequently, they were adsorbed on CuO from a solution of pH ≈ 10 in preparation of the samples for TDPAC measurement.

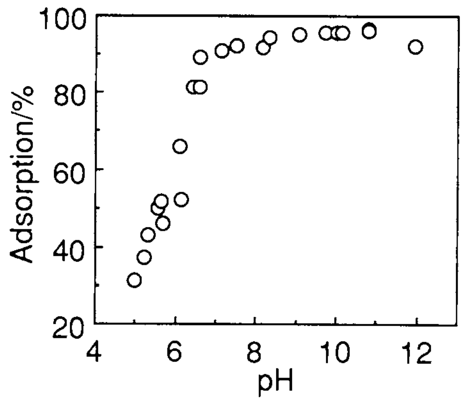

Fig. 2. Adsorption yield of carrier-free $^{99}Rh^{3+}$ ions on CuO from a 0.1 mol dm^{-3} NaCl solution (equilibration time was 2 h).

Stoichiometric amounts of dried high-purity powders of CuO with adsorbed $^{99}Rh^{3+}$, Y_2O_3, and $BaCO_3$ were milled, and the mixture was heated in flowing oxygen at 200 °C for 1 h, then up to 890 °C at a rate of 3.8 °C/min, and was kept at that temperature for 6.5 h. The product was repowdered and pressed into a pellet. It was heated at 950 °C for 6 h and annealed at 550 °C for 15 h in oxygen. The powder X-ray diffraction pattern of undoped $YBa_2Cu_3O_{7-x}$ prepared by the same heating process was typical of the ortho-I phase. Both the doped and undoped samples showed the Meissner effect at liquid nitrogen temperature. The x value was estimated to be about 0.2 by iodometry. A sample with a higher x value was prepared by heating the above one at 760 °C for 1 h under a reduced pressure of about 2 Pa. The x value of the sample obtained was about 1.0.

The TDPAC spectra of γ-rays of ^{99}Ru arising from ^{99}Rh in the samples were measured in the temperature range from 10 to 1173 K. The γ-rays employed for the measurement were the 353 - 90 keV cascade through the intermediate 3/2+ level with a half-life of 20.5 ns (Fig. 1). The TDPAC spectrometer was comprised of four 38 mm $\phi \times$ 25 mm BaF_2 scintillators mounted on Hamamatsu R2059 photomultipliers, conventional fast-slow circuits, and a multichannel analyzer connected to a personal computer. The time resolution of the spectrometer was 350 ps with the energy windows of single-channel analyzers set at 1173- and 1333-keV γ-rays of ^{60}Co. Coincidence counts, N, for a detector combination with angles π/2 and π rad were measured as a function of the time (t) elapsed between the detection of 353- and 90-keV γ-rays. Four spectra, two for π/2 rad and two for π, were taken simultaneously and were processed together to yield the TDPAC spectrum:

$$A_{22}G_{22}(t) = 2[N(\pi,t)-N(\pi/2,t)]/[N(\pi,t)+2N(\pi/2,t)].$$

Figures 3 and 4 show typical TDPAC spectra obtained (left) and their frequency spectra (right) for the two samples prepared. As can be seen in Fig. 3(b), the frequency spectra of the sample with x ≃ 0.2 have two distinct peaks. These peaks are attributed to electric quadrupole frequencies of ^{99}Ru with different ligand oxygen configurations. However, only one significant peak was observed in the frequency spectra of the $YBa_2Cu_3O_{7-x}$ sample with x ≃ 1.0 (Fig. 4(b)). The spectrum of the sample at 10 K is broadened, indicating an additional hyperfine interaction on ^{99}Ru nuclei at that temperature. We ascribe the origin of the broadening to a hyperfine magnetic interaction of the ^{99}Ru nuclei with magnetically ordered Cu ions. At 293 K, the width of the dominant peak is much smaller, though trailing in the low-frequency side is observed.

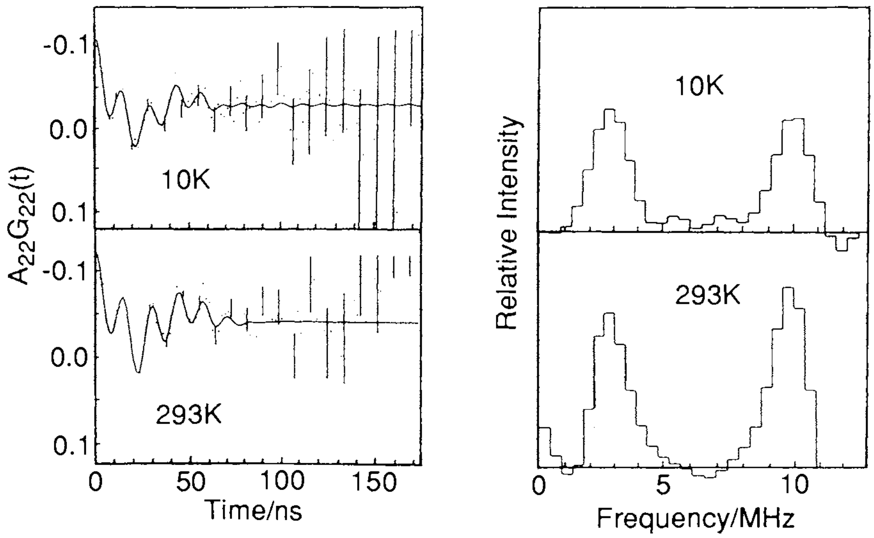

Fig. 3. Typical TDPAC spectra of γ-rays of ^{99}Ru arising from ^{99}Rh in $YBa_2Cu_3O_{7-x}$ with x ≃ 0.2 (left) and their frequency spectra (right).

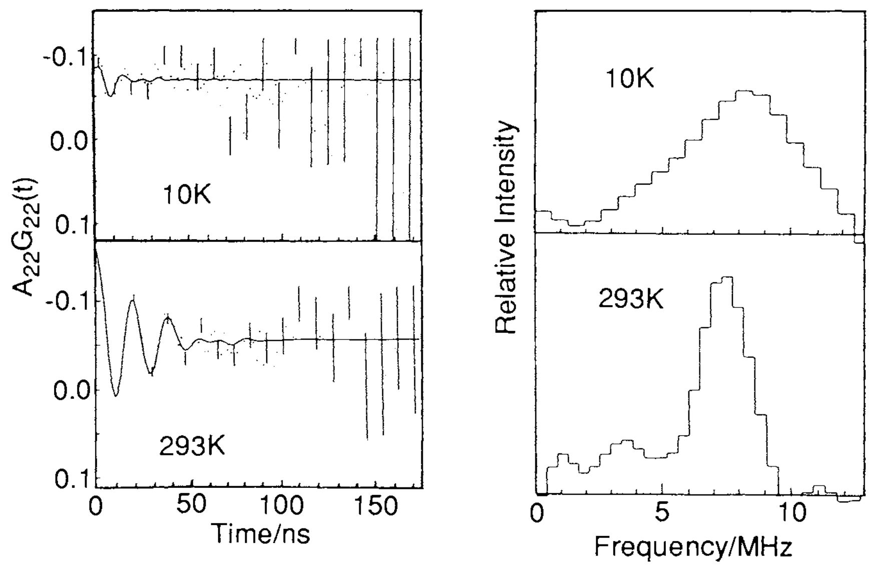

Fig. 4. Typical TDPAC spectra of γ-rays of ^{99}Ru arising from ^{99}Rh in $YBa_2Cu_3O_{7-x}$ with x ≃ 1.0 (left) and their frequency spectra (right).

Antiferromagnetic ordering of the tetragonal phase of $YBa_2Cu_3O_{7-x}$ was first demonstrated by μSR, and the ordering was ascribed to Cu-2 atoms.[11] Neutron-diffraction experiments confirmed its antiferromagnetic structure with the Néel temperature ≥ 500 K for x = 1.0, and a model with antiparallel spins at the Cu-2 sites was proposed.[12] Mössbauer measurements of hyperfine magnetic fields on ^{57}Fe doped in an oxygen-deficient $YBa_2Cu_3O_{7-x}$ sample showed that the magnetic transition temperature T_N of Cu-2 planes is as high as 420 K, while T_N of the Cu-1 sites is much lower than that.[1] Therefore, we conclude that Ru ions occupy the Cu-1 site in our $YBa_2Cu_3O_{7-x}$ sample with x ≃ 1.0 on the basis of the observed temperature dependence of the TDPAC spectrum. Further work is in progress to determine the site position of ^{99}Ru in the $YBa_2Cu_3O_{7-x}$ sample with x ≃ 0.2.

In conclusion, ^{99}Ru has been shown to be a useful hyperfine-interaction probe comparable to ^{57}Fe concerning the investigation of superconducting materials. Detailed discussion on the present experimental results will be presented elsewhere with additional results including those of emission Mössbauer measurement of the same sample.

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