Studies of ^{99}Ru ions in metal oxides by means of time-differential perturbed-angular correlation and emission Mössbauer measurements

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Radioactive ^{99}Rh ions were incorporated into α-Fe_2O_3, Fe_3O_4, and $YBa_2Cu_3O_6$ with the aid of radiochemical techniques, and the site of ^{99}Ru occupying and the valence of the Ru ion in each compound were determined by means of TDPAC and Mössbauer spectroscopy. It was observed that the valences of the Ru ions in α-Fe_2O_3 and Fe_3O_4 are unusually low, while it is normal in $YBa_2Cu_3O_6$. An idea concerning the valence of a Ru ion in oxides is proposed.

Introduction

The radioactive isotope ^{99}Rh is very useful for the studies of hyperfine interacions: it serves as the source nuclide of Mössbauer spectroscopy on ^{99}Ru as well as of γ-γ time-differential perturbed-angular correlation (TDPAC). A simplified decay scheme of ^{99}Rh is shown in Fig. 1. Both TDPAC and emission Mössbauer measurements can be performed on the same sample with dilutely incorporated ^{99}Rh. Unlike TDPAC, ^{99}Ru-Mössbauer spectroscopy can be applied only at low temperatures because the energy of Mössbauer γ rays from the first excited state (the intermediate state in TDPAC) is as high as 90 keV. However, the isomer shift obtained by ^{99}Ru-Mössbauer spectroscopy provides information on the valence of Ru, which is not accessible by TDPAC. In the present work, we incorporated ^{99}Rh ions into α-Fe_2O_3, Fe_3O_4, and $YBa_2Cu_3O_6$, and determined the site where ^{99}Ru occupies and the valence of the Ru ion in each compound by means of TDPAC and Mössbauer spectroscopy. α-Fe_2O_3 has the corundum structure and is antiferromagnetic below $T_N = 950$ K. Fe_3O_4 is an inverse spinel and is a ferrimagnet with $T_C = 858$ K. The oxygen ions in both iron oxides are close-packed. $YBa_2Cu_3O_6$ is an oxygen-deficient perovskite-like oxide, in which there are two kinds of copper sites, Cu-1 and Cu-2. From the ionic radius of Rh^{3+}, it is expected that Rh ions substitute Fe ions in iron oxides and Cu ions in $YBa_2Cu_3O_6$.

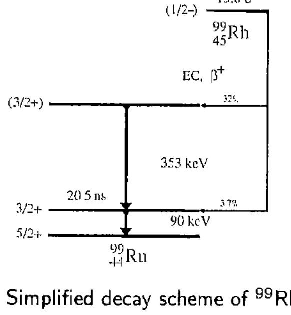

Fig. 1. Simplified decay scheme of ^{99}Rh→^{99}Ru.

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Experimental procedures

Sample preparations About 97% enriched ^{99}Ru was irradiated with 12- or 13-MeV protons available from the RIKEN 160-cm cyclotron or the INS-SF cyclotron. A carrier-free aqueous solution containing $^{99}Rh^{3+}$ was obtained from the irradiated Ru target by radiochemical separation.[1] For the preparation of iron oxides, ^{99}Rh in the solution was coprecipitated with ferric hydroxide. The precipitate was dried and then heated in air at 900 °C, and α-Fe_2O_3(^{99}Rh) was thereby obtained.[2] In order to obtain Fe_3O_4(^{99}Rh), α-Fe_2O_3(^{99}Rh) was heated under reduced pressure at 1150 °C.[1] For the preapration of $YBa_2Cu_3O_6$, CuO powder was added to the aqueous solution containing ^{99}Rh to let it adsorb the rhodium ions. Stoichiometric amounts of high purity of Y_2O_3, $BaCO_3$, and dried CuO with ^{99}Rh were milled, heated in oxygen at 950 °C, and then heated under reduced pressure at 760 °C.[3,4]

TDPAC and emission Mössbauer measurements The time spectra $N(\theta, t)$ of the 353-90 keV γ-γ cascade emitted from the excited states of ^{99}Ru were taken with a fast-slow setup with 25.4 mm-thick BaF_2 scintillators. θ and t denote the angle and the time interval, respectively, between the cascade γ rays. The four detector system was employed to obtain the directional anisotropy, $A_{22}G_{22}(t)$, defined by Eq. (1).

$$A_{22}G_{22}(t) = 2[N(\pi, t) - N(\pi/2, t)]/[N(\pi, t) + 2N(\pi/2, t)]. \quad (1)$$

Two detectors were used for detecting 353-keV γ rays, and the other two for detecting 90-keV γ rays.

For an ensemble of randomly oriented microcrystals with a unique static interaction, $G_{22}(t)$ is generally a function of the following quantities through the interaction Hamiltonian: the Larmor frequency ω_L, the electric quadrupole frequency

ω_Q, the asymmetry parameter η of the electric field gradient (EFG), and the angles, θ and φ, describing the direction of the hyperfine magnetic field H_{hf} in the spherical coordinate system fixed to the principal axes of the EFG. When the interaction Hamiltonian consists only of a hyperfine magnetic interaction term,

$$A_{22}G_{22}(t) = A_{22}[1 + 2\cos(\omega_L t) + 2\cos(2\omega_L t)]/5. \qquad (2)$$

When the interaction Hamiltonian consists only of an axially symmetric quadrupole interaction term,

$$A_{22}G_{22}(t) = A_{22}[1 + 4\cos(6\omega_Q t)]/5. \qquad (3)$$

^{99}Ru-emission Mössbauer spectra were obtained at 5 K with a conventional apparatus with a 2 mm-thick NaI(Tl) scintillator. The sample containing ^{99}Rh as a source was mounted on the driver, and enriched ^{99}Ru was used as an absorber.

Results

As an example, $A_{22}G_{22}(t)$ of ^{99}Ru in Fe_3O_4 at various temperatures, including a temperature above T_C, are shown in Fig. 2(a). Figure 2(b) shows the frequency distributions of $A_{22}G_{22}(t)$. The frequency spectra obtained below T_C have two peaks. The ratio of frequencies at the two peaks are one to two, which is well described by Eq. (2). These mean that the dominant hyperfine interaction at ^{99}Ru in Fe_3O_4 is magnetic. In the frequency spectrum of $A_{22}G_{22}(t)$ obtained at 885 K, there is only one peak at $\omega = 0$ with a width ascribable to the quadrupole frequency, $6\omega_Q$ [see Eq. (3)]. Therefore, at temperatures below T_C there should be a small EFG at ^{99}Ru in Fe_3O_4 in addition to the large H_{hf}. The temperature dependence of H_{hf} suggests that there are two origins for the observed H_{hf}: the major part is produced by the magnetic moments of Fe^{3+} via the supertransfer mechanism, and the minor one by that of the unpaired 4d electron of the ^{99}Ru ion itself.[1] The sign of ω_L was determined at room temperature by TDPAC, the experimental setup consisting of three detectors. Two detectors were placed at angles of $\pm 135°$ with respect to a detector, and an external magnetic field was applied perpendicular to the detector plane. From the negative sign of ω_L, we confirmed that ^{99}Rh ions are in the octahedral sites of Fe_3O_4.[1] In similar ways we confirmed that ^{99}Rh ions substitute Fe ions in α-Fe_2O_3[2] and exclusively Cu ions at the Cu-1 sites in $YBa_2Cu_3O_6$.[4] The isomer shifts of ^{99}Ru in α-Fe_2O_3, Fe_3O_4, and $YBa_2Cu_3O_6$ were determined to be −0.58, −0.76, and −0.26 mm/s, respectively, from the Mössbauer spectra obtained at 5 K.

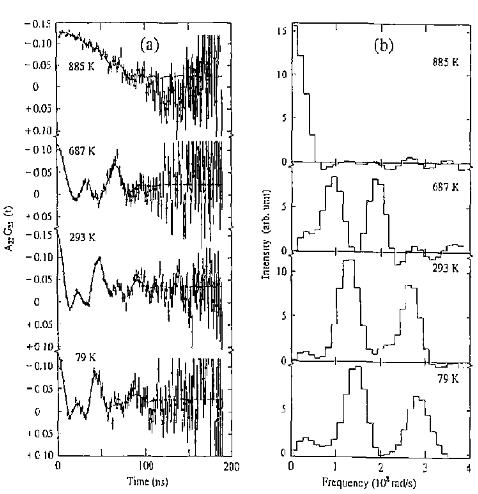

Fig. 2. (a) TDPAC spectra, $A_{22}G_{22}(t)$, of ^{99}Ru($\leftarrow ^{99}$Rh) in Fe_3O_4 measured at 79 K, 293 K, 687 K, and 885 K, and (b) their frequency distributions. The solid curves in (a) represent the time spectra reproduced from the frequency distributions in (b).

Discussion

The isomer shift of ^{99}Ru correlates with the valence of ruthenium in oxides,[1] as shown in Fig. 3. According to this figure, the valence of ^{99}Ru in α-Fe_2O_3, Fe_3O_4, and $YBa_2Cu_3O_6$ can be assigned to be +3, +2 $\sim$ +3, and +4, respectively. The temperature dependence of H_{hf} at ^{99}Ru in Fe_3O_4 and the extraporated value at 0 K indicate that the valence of the Ru ion in this oxide cannot exactly be +2 or +3. Therefore, the above description +2 $\sim$ +3 means that the Ru ion in Fe_3O_4 exists as a mixed state of Ru^{2+} and Ru^{3+}. Considering that the minimum valence of a Ru ion in its pure oxides is +4, the valences of the Ru ions in α-Fe_2O_3 and Fe_3O_4 are unusually low, while it is normal in $YBa_2Cu_3O_6$. We notice that the valences of the Ru ions in α-Fe_2O_3 and Fe_3O_4 coincide with those of the substituted Fe ions. We propose the following idea. Dilutely incorporated Ru ions have a tendency to take the same valence as metal ions in the matrix do in the following conditions: 1) oxygen ions are close-packed; 2) the coordination number of Ru ions is the same as that for metal ions. For α-Fe_2O_3 and Fe_3O_4, both conditions hold. For $YBa_2Cu_3O_6$ the first condition does not hold. Since the average valence of the Cu ion at the Cu-1 site is +2.5 and low, the Ru ion is considered to take the minimum valence in its pure oxide, +4. We are going to test our idea by measuring the isomer shift of ^{99}Ru in NiO or CoO, for example.

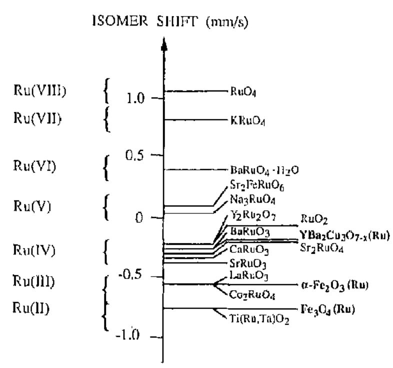

Fig. 3. Systematics of isomer shifts of ^{99}Ru in oxides. The data are taken from references cited in Ref. 1.

References

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