^{89}Y NMR study of the exchange coupling constant between the CuO_2 layer and the Gd ion in $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$

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Free-induction decays of ^{89}Y NMR are observed in magnetically dilute alloys $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ for $x=0$, 0.005, and 0.01. It is shown that the excess decay by Gd is almost completely due to its direct dipolar interactions. From an analysis of the indirect Ruderman-Kittel-Kasuya-Yosida interaction, the exchange coupling constant is estimated to be less than 0.01 eV.

In the superconducting compounds $YBa_2Cu_3O_{7-\delta}$ the substitution of the Y ion for most rare-earth elements has no influence to the superconducting state.[1] It is therefore considered that the coupling is weak between a Y layer and a CuO_2 layer having the essential role of superconductivity. However, the exact knowledge of the coupling will be required to understand the interaction that is responsible for the antiferromagnetic ordering of rare-earth magnetic moments in $RBa_2Cu_3O_{7-\delta}$, where R is a rare-earth element.[2] As possible mechanisms of the ordering, the direct dipole-dipole interaction and the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction via conduction electrons in the CuO_2 layer are considered, which is, however, still controversial.[2-4]

Information on the exchange coupling constant J, between the conduction electron and the rare-earth magnetic moment, can be obtained by analyzing the influence of the RKKY interaction on ^{89}Y NMR signals in magnetically dilute alloys $R_xY_{1-x}Ba_2Cu_3O_{7-\delta}$. Since the spin of the ^{89}Y nucleus is $\frac{1}{2}$ and no complexity due to quadrupole moments is present, the ^{89}Y nucleus is suitable for probes to investigate the magnetic interactions. In the present work we measured the ^{89}Y NMR in $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ ($x=0$, 0.005, and 0.01), where Gd concentrations are 0, 0.5, and 1 at.%, respectively. Although the value of J is expected to be very small, we tried to estimate its upper limit within the results of the ^{89}Y NMR measurements.

The samples were prepared with the citric-acid method[5] to obtain homogeneous mixtures of appropriate quantities of Y, Ba, Cu, and Gd. The homogeneity of constituents is especially important to our samples containing a very small amount of Gd atoms. The mixtures were fired at 800°C for 10 h and then ground. The powders were pressed into pellets, sintered in air at 930°C for 10 h, and then annealed in O_2 atm at 450°C for 24 h. After four repetitions of this process, they were quenched to room temperature. The pellets, of which superconducting transitions were observed at 92 K (zero resistance temperature), were reground and packed into glass tubes. Each of them contained about 2 g of the powder sample. We observed free-induction decays (FID) after a 90° pulse at 10.7 MHz by using a usual pulse method. All measurements were performed at 100 K, where the samples were in the normal state. The static field of about 5 T was applied by a superconducting magnet. The signals were accumulated for 2–10 h because the signal-to-noise ratio was poor.

Figure 1(a) shows the FID of ^{89}Y NMR for $YBa_2Cu_3O_{7-\delta}$. The time for which the intensity of the FID decreased to $1/e$ (T_2^*) was about 0.3 ms and the spin-spin relaxation time (T_2) obtained by the spin-echo method was about 6 ms. These values were consistent with the results by Markert *et al.*[6] The FID's for $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ ($x=0.005$ and 0.01) are shown in Figs. 1(b) and 1(c) with solid lines. We notice that the decay time constant of the FID decreases with increasing x. The local field, which causes the decay on the Y nucleus, consists of two parts: H_d and H_{RKKY}. For $x=0$, H_d is the local field due to the dipolar interactions with both Y and Cu nuclear magnetic moments. For $x\neq 0$, in addition to Y and Cu, the dipolar interactions with Gd electronic mag-

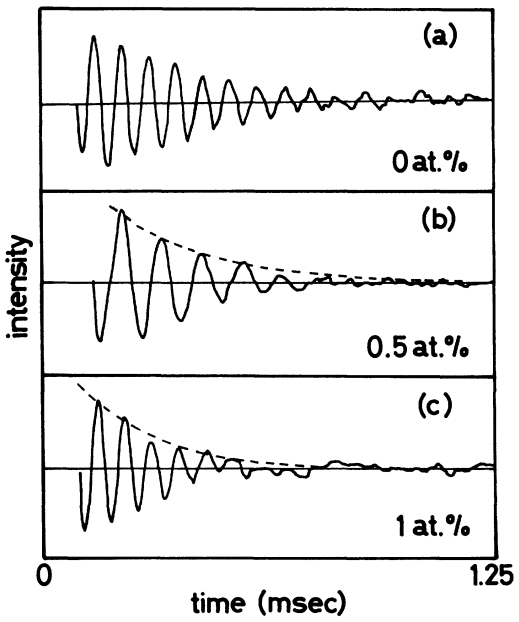

FIG. 1. Solid lines are FID's of ^{89}Y NMR in the magnetically dilute alloys $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ at 100 K. The beat is due to a difference between the Larmor and the rf frequency. Necessary information is the decay time constant of the intensity and not the presence of the beat. Dashed lines are calculated decay curves from the dipolar local fields. (a) $x=0$, (b) $x=0.005$, and (c) $x=0.01$.

netic moments also contribute to H_d. H_{RKKY} is due to the RKKY interaction in which a nuclear magnetic moment of Y couples indirectly with electronic ones of Gd via a conduction-electron spin polarization in the CuO_2 plane. The above-mentioned decrease of the decay time constant with an increase of the Gd concentration x shows the effect of the local fields originating from the Gd moments.

For 0.5 and 1 at.% of Gd concentration, we obtained the predicted decay curves as the product of a curve which fitted to the decay of the FID for $x=0$ and a curve whose decay was due to only the dipolar fields of the Gd electronic spins. The latter curve was calculated with the assumption that Gd ions were randomly distributed in the Y layer after the method by Walstedt and Walker[7] to calculate field distributions in magnetically dilute alloys. The obtained curves are given in Figs. 1(b) and 1(c) (dashed lines). They fit the observed decays very well. Consequently, it is considered that the H_d dominates the decay and that the H_{RKKY} is negligibly small, as is expected.

Our next discussion is to evaluate the J value by calculating the local field due to the RKKY interaction. The expression of H_{RKKY} is given by Yosida in three dimensions.[8] However, a two-dimensional expression of H_{RKKY} is required for this analysis because conduction electrons exist in CuO_2 planes in the materials. Taking into account some discussions,[9,10] we obtained the following expression for the two-dimensional H_{RKKY}:

$$H_{RKKY}=\frac{|\langle S_z\rangle|}{\gamma\hbar}\left(\frac{n}{N}\right)^2\frac{2}{E_F}AJ \times\sum_m\left[\frac{\sin(2k_FR_m)}{(k_FR_m)^2}-\frac{13}{16}\frac{\cos(2k_FR_m)}{(k_FR_m)^3}\right]. \quad (1)$$

The direction of the applied magnetic field is along the z axis and R_m is the distance from a Y nucleus at the origin to the mth Gd ion. A is the hyperfine coupling constant between a magnetic moment of Y and a conduction electron, and its value was obtained from the result of the Knight shift measurement.[11] E_F, Fermi energy, was estimated from its two-dimensional relation to the Pauli susceptibility χ_p (Ref. 11) and then k_F, Fermi wave vector, was calculated from E_F, where the free-electron band was assumed. $2n$ and N are the total number of carriers and that of lattice sites, respectively, and n/N was obtained with the value of $2n$ for $\delta=0$. The averaged magnitude of the spin of the Gd ion $|\langle S_z\rangle|$ was calculated on the assumption that the Curie law was valid. Their numerical values are listed in Table I. The formula in the summation is an expansion of the exact solution to the second term. Although this asymptotic form is invalid when the magnitude of k_FR_m is small, this approximation was used to calculate the contributions of all Gd sites, because there are few sites near the origin compared with the total number of lattice sites and they have a statistically lower weight. After the method by Mizuno,[12] we calculated the local-field distribution density of H_{RKKY} in Eq. (1) regarding the unknown J as a parameter.

The result of this calculation gives an absorption linewidth broadened by H_{RKKY}. In general, an absorption line is a Fourier transform of a FID, and vice versa. In order to compare the calculated linewidths with the experimental decay rates, the half-width for the FID was obtained as a reciprocal of the decay time constant. The full width at half maximum of each calculated line shape is shown in Fig. 2 as a function of the concentration of Gd. The results for 0.1 and 0.2 at.% are also given there, but they are not used in this discussion.

We thought that if the calculated width was larger than $\frac{1}{10}$ of the width estimated from the observed FID (Fig. 1), there would be a significant difference between the FID and the decay curve calculated from only the dipolar local field. Since there was no difference between them as seen in the preceding discussion, the width due to the RKKY interaction was estimated not be be larger than $\frac{1}{10}$ of the observed width. The calculated widths are $74J$ Oe for 0.5 at.% and $110J$ Oe for 1 at.% from Fig. 2, while the widths from the FID's are 5.6 and 8.6 Oe for 0.5 and 1 at.%, respectively. Thus, the following inequalities were obtained,

$$74J<\tfrac{5.6}{10}\ (0.5\ \text{at.}\%),$$

$$110J<\tfrac{8.6}{10}\ (1\ \text{at.}\%),$$

and from them

$$J<0.01\ (\text{eV}).$$

As a result, we estimated the upper limit of the J value to be 0.01 eV. This value is compared with 0.3 eV for Gd in Ag,[13] for example. It is found that the J in the present material is smaller than that in AgGd by more than 1 order of magnitude.

TABLE I. Numerical values used in the calculation of the local-field distribution density of H_{RKKY}.

A	E_F	k_F	n/N	$\lvert\langle S_z\rangle\rvert$
3.9×10^{-9} eV	0.3 eV	2.7×10^{7} cm^{-1}	0.5	0.36

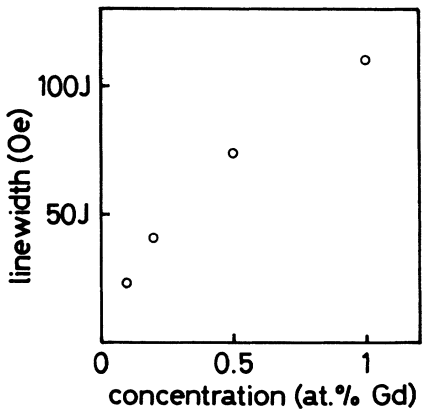

FIG. 2. Calculated linewidths due to the RKKY interaction as a function of the concentration of Gd. Each of them is obtained as a full width at half maximum of the local-field distribution density of H_{RKKY}. The exchange coupling constant J enters as a parameter. The data for 0.1 and 0.2 at.% are not used in the text.

In summary, we observed the ^{89}Y NMR in the magnetically dilute alloys $Gd_xY_{1-x}Ba_2Cu_3O_{7-\delta}$. The decay of the signal is caused only by the dipolar local fields, and the RKKY interaction is not effective. The exchange coupling constant J is less than 0.01 eV.

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