^{155}Gd Mössbauer Spectroscopic Study of $GdM(CN)_6 \cdot 4H_2O$ (M = Cr^{III}, Fe^{III} and Co^{III}) and $KGdM(CN)_6 \cdot 3H_2O$ (M = Fe^{II} and Ru^{II})

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^{155}Gd Mössbauer spectroscopic studies of the title complexes have been performed. Although the ^{155}Gd isomer shifts (δ) varied scarcely, the quadrupole coupling constants (e^2qQ) changed in the range 4.07–4.81 mm s^{-1}. The e^2qQ values of $KGdM(CN)_6 \cdot 3H_2O$ (M = Fe^{II} and Ru^{II}) are larger than those of $GdM(CN)_6 \cdot 4H_2O$ (M = Cr^{III}, Fe^{III}, and Co^{III}), these values increasing with increasing orthorhombic distortion of the crystal structures. A relationship between the e^2qQ values and the ionic radii of the transition metal ions has also been recognized.

Key words: ^{155}Gd Mössbauer Spectroscopy; Quadrupole Coupling Constant; Gd(III) Cyano Polymeric Complex; Orthorhombic Distortion.

1. Introduction

Many gadolinium compounds, including solid solutions, intermetallic compounds, alloys and oxides have been studied by ^{155}Gd Mössbauer spectroscopy [1]. Among the ^{155}Gd Mössbauer parameters, especially the quadrupole coupling constant (e^2qQ) gives a valuable information. However, such studies on the structural and bonding properties of Gd(III) coordination compounds have scarcely been done, and therefore we have started a systematic study of these.

Since the cyano group is able to behave as a bridging ligand, various assembled metal complexes have been synthesized. Among a number of cyano assembled metal complexes, the rare-earth hexacyanometalate(III) $LnM(CN)_6 \cdot nH_2O$ (Ln = rare-earth ion, M = transition metal ion) and the rare-earth hexacyanometalate(II) $KLnM(CN)_6 \cdot nH_2O$ have been studied because of their interesting structural and magnetic properties [2–8]. Hexagonal $LnM(CN)_6 \cdot 5H_2O$ is formed with larger Ln ions such as La^{3+}, Ce^{3+}, and orthorhombic $LnM(CN)_6 \cdot 4H_2O$ with smaller Ln ions such as Sm^{3+}, Gd^{3+}. Both complexes consist of infinite arrangements of octahedral transition metal M(III) ions and eight coordinated rare-earth Ln(III) ions. The cyano group behaves as a bridging ligand and coordinates to the Ln(III) ion by the nitrogen atom. The three dimensional polymeric structure of $GdFe(CN)_6 \cdot 4H_2O$ [4] is shown in Fig. 1 as an example. The coordination geometry of the Gd(III) ion is a square antiprism since two water molecules are coordinated to one Gd atom. $KLnM(CN)_6 \cdot 3H_2O$ is a substitutional derivative of $LnM(CN)_6 \cdot 4H_2O$, in which the potassium ions replace statistically half of the zeolitic water molecules [7–8].

^{57}Fe and ^{151}Eu Mössbauer spectroscopic studies of these rare-earth cyano assembled metal complexes have been reported by several groups [9–13]. The ^{57}Fe Mössbauer parameters, especially quadrupole splitting (Q. S.), give useful information on the distortion of the octahedral iron sites [9]. Katada et al. reported that the ^{57}Fe Mössbauer Q. S. values are associated with the orthorhombic distortion in their crystal structures for the $LnFe(CN)_6 \cdot 4H_2O$ (Ln = Sm-Lu) series [13].

We report here a ^{155}Gd Mössbauer spectroscopic study of five Gd(III) cyano polymeric complexes: $GdFe(CN)_6 \cdot 4H_2O$ **I-1**, $GdCo(CN)_6 \cdot 4H_2O$ **I-2**, $GdCr(CN)_6 \cdot 4H_2O$ **I-3,** $KGdFe(CN)_6 \cdot 3H_2O$ **II-1** and $KGdRu(CN)_6 \cdot 3H_2O$ **II-2**. e^2qQ is found to increase with increasing orthorhombic distortion. A relation between the e^2qQ values and the ionic radii of the transition metal ions is also recognized.

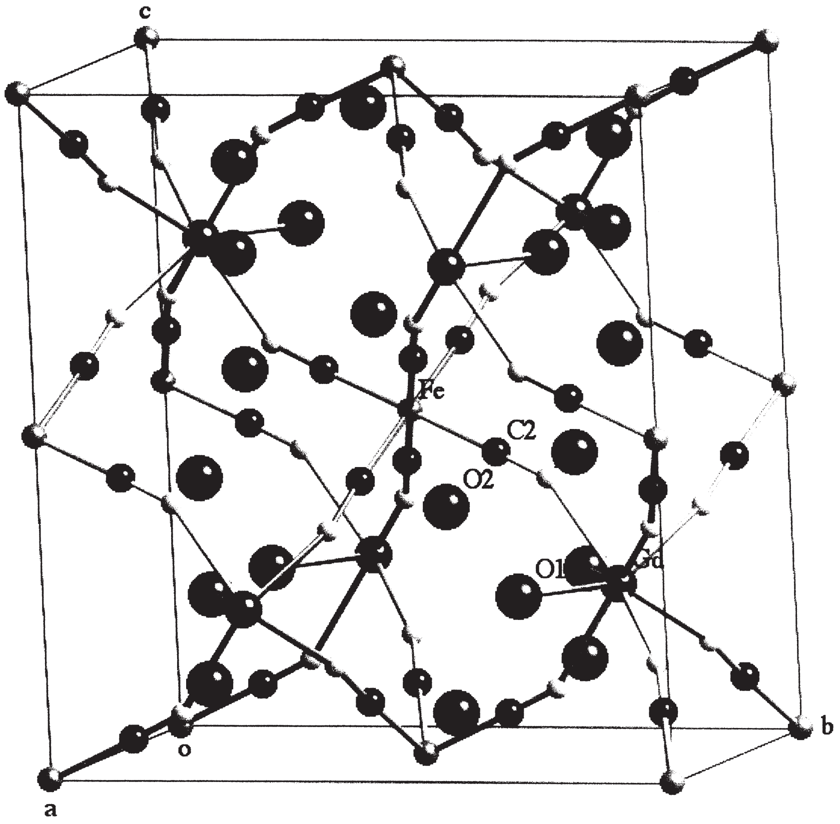

Fig. 1. Crystal packing diagram of $GdFe(CN)_6 \cdot 4H_2O$ **I-1** [4]. An eight-coordinate structure about Gd is made of six nitrogen atoms (N) of the cyano group and two coordinated oxygen atoms (O1) of waters. O2 is an oxygen atoms of zeolitic water.

2. Experimental

2.1. Preparation of the Materials

All of the complexes were prepared by a procedure similar to that of Prandtl and Mohr [14]. A typical procedure is described for **I-1**: In 50 ml of distilled water, 1.86 g (5 mmol) of $GdCl_3 \cdot 6H_2O$ and 1.46 g (5 mmol) of $K_3Fe(CN)_6$ were dissolved. The solution was filtered and stored in a dark place at room temperature. Dark red powder crystals were formed after only several minutes. For **I-2**, **I-3**, **II-1** and **II-2** the solutions were prepared in the same manner using $K_3Co(CN)_6$, $K_3Cr(CN)_6 \cdot 3H_2O$, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_4Ru(CN)_6 \cdot 3H_2O$ as the transition metal source.

The five complexes were identified by powder X-ray diffraction (XRD), Infrared spectroscopy (IR) and chemical analysis. The obtained lattice parameters are identical with the reported data [5–7].

2.2. Preparation of the ^{155}Gd Mössbauer Source $^{155}Eu/^{154}SmPd_3$

$^{155}Eu/^{154}SmPd_3$ was prepared by a modified method of Cashion et al. [15]. $^{154}SmPd_3$ alloy was prepared by sintering a mixture of $^{154}Sm(HCOO)_3$ and PdH_x (Sm : Pd = 1 : 3) at 1273 K for 18 hours in a hydrogen atmosphere. The $^{154}SmPd_3$ alloy was pressed into a disk, sealed with highly-pure aluminum foil, and irradiated in the HR-2 hole of a JRR-3M reactor (neutrons flux: 6.0×10^{13} cm^{-2} s^{-1}) of JAERI for 67 hours. After cooling for about three months, the $^{155}Eu/^{154}SmPd_3$ (about 231 MBq) was used as the source.

2.3. ^{155}Gd Mössbauer Measurement

The ^{155}Gd Mössbauer spectra were measured by the $^{155}Eu/^{154}SmPd_3$ source on a WissEl Mössbauer measuring system consisting of MDU-1200, DFG-1200 and MVT-1000. Both of the source and the sample, containing 115 mg Gd cm^{-2}, were kept at 12 K in a cryostat equipped with a closed-cycle refrigerator. The 86.5 keV

γ-rays were counted with a pure germanium detector. The Doppler velocity was measured with a laser Mössbauer velocity calibrator WissEl MVC-450. The velocity was calibrated by measuring a ^{57}Fe Mössbauer spectrum of an α-iron foil. The ^{155}Gd Mössbauer spectra were computer-fitted to quadrupole-split five-lines ($I_g - I_e$ = 3/2–5/2, η = 0) using the sum of the Lorentz approximations [16]. The quadrupole moments used for the ground and excited state of the ^{155}Gd Mössbauer transition were Q_g = 1.50 b and Q_e = 0.18 b, respectively [17]. The value of the ^{155}Gd isomer shift (δ) is referred to the ^{155}Eu/^{154}SmPd$_3$ source at 12 K.

3. Results and Discussion

Our method for preparing the ^{155}Eu/^{154}SmPd$_3$ source is simpler than that reported by Cashion et al. [15]. Cashion et al. synthesized the ^{154}SmPd$_3$ alloy by the following method: the ^{154}Sm$_2$O$_3$ is converted to ^{154}Sm(HCOO)$_3$, intimately mixed with the stoichiometric amount of PdH$_x$ powder, compressed to a pellet, dissociated in vacuum, melted in an argon-arc furnace and then annealed. We prepared the ^{154}SmPd$_3$ alloy only by sintering the mixture of ^{154}Sm(HCOO)$_3$ and PdH$_x$ (Sm : Pd = 1 : 3) at 1273 K for 18 hours in the hydrogen atmosphere. Our results indicate that a fine source as good as that of Cashion et al. can be obtained by our simpler synthesizing method for the ^{154}SmPd$_3$ alloy.

The measured ^{155}Gd Mössbauer spectra for **I-1**, **I-2**, **I-3**, **II-1** and **II-2** at 12 K are shown in Figure 2. The ^{155}Gd Mössbauer parameters δ, e^2qQ and the line-width (2Γ) are listed in Table 1. All the spectra have the typical pattern of electric quadrupole splitting of ^{155}Gd Mössbauer spectroscopy, where the apparently observed doublet is a consequence of the dominance of the nuclear quadrupole moment of the ground state [1]. Although our ^{155}Gd δ values are almost the same within the experimental error, ~0.60 mm s^{-1}, the e^2qQ values are spread out from 4.07 mm s^{-1} to 4.81 mm s^{-1}.

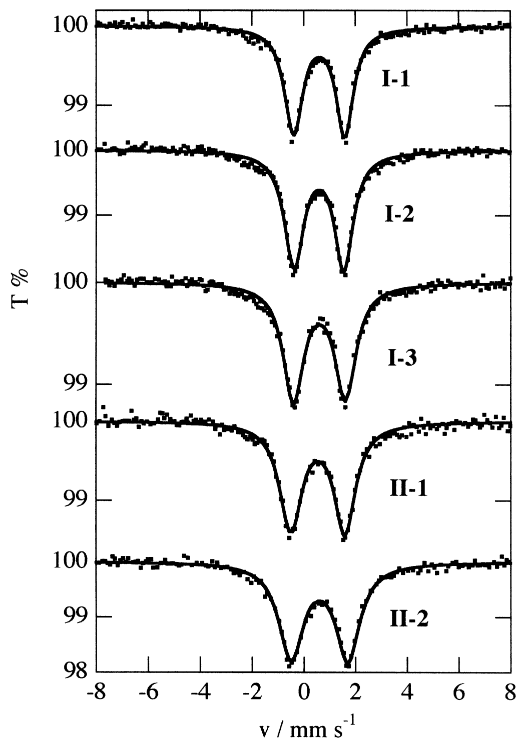

Fig. 2. ^{155}Gd Mössbauer spectra at 12 K for the five Gd(III) cyano polymeric complexes. **I-1**: GdFe(CN)$_6$ · 4H$_2$O, **I-2**: GdCo(CN)$_6$ · 4H$_2$O, **I-3**: GdCr(CN)$_6$ · 4H$_2$O, **II-1**: KGdFe(CN)$_6$ · 3H$_2$O and **II-2**: KGdRu(CN)$_6$ · 3H$_2$O.

Table 1. ^{155}Gd Mössbauer parameters of cyano polymeric complexes at 12 K: GdFe(CN)$_6$ · 4H$_2$O **I-1**, GdCo(CN)$_6$ · 4H$_2$O **I-2**, GdCr(CN)$_6$ · 4H$_2$O **I-3**, KGdFe(CN)$_6$ · 3H$_2$O **II-1** and KGdRu(CN)$_6$ · 3H$_2$O **II-2**.

Complex	δ* mm s^{-1}	e^2qQ mm s^{-1}	2Γ mm s^{-1}
I-1	0.61	4.07	0.90
I-2	0.60	4.12	0.87
I-3	0.61	4.30	1.04
II-1	0.59	4.68	1.01
II-2	0.60	4.81	0.93

(Error δ: ± 0.02 mm s^{-1}, e^2qQ and 2Γ: ± 0.05 mm s^{-1}.)
* Relative to the ^{155}Eu/^{154}SmPd$_3$ source at 12 K.

The results of δ indicate that the *s*-densities at the Gd nucleus are almost the same for the five Gd(III) cyano polymeric complexes. The δ values are in the range of those of Gd(III) coordination compounds, such as Gd(III)-EDTA [18] and Gd(III)-β-diketonato complexes [19]. Katada et al. have reported that the ^{151}Eu Mössbauer δ of EuFe(CN)$_6$ · 4H$_2$O is smaller than that of KEuFe(CN)$_6$ · 4H$_2$O [11]. However, δ for ^{155}Gd of GdFe(CN)$_6$ · 4H$_2$O (**I-1**) almost equals that of KGdFe(CN)$_6$ · 3H$_2$O (**II-1**). The difference between the Gd and Eu system may be associated with the difference of $\Delta R/R$, where R is nuclear radius.

The ^{155}Gd δ values of the Gd(III) cyano polymeric complexes, [Gd(III)-β-diketonato complexes (δ = 0.55 ~

0.65 mm s^{-1}), Gd(III)-EDTA complexes ($\delta = 0.60\sim0.62$ mm s^{-1})] indicate that the difference in the δ values for the Gd(III) coordination compounds is smaller than that for the gadolinium intermetallic compounds reported (–0.2 ~ 0.9 mm s^{-1}) [1]. A systematic investigation on the applicability of the δ value in the Gd(III)-β-diketonato complexes, Gd(III) EDTA complexes and Gd(III) cyano polymeric complexes is in progress.

The e^2qQ values decrease in the order **II-2** > **II-1** > **I-3** > **I-2** ≈ **I-1**, as shown in Figure 3. This indicates that the electric field gradient (EFG) at the Gd atom decreases in this order. In general, the EFG is produced by charges at greater distance (the lattice EFG) and by valence electrons (the valence EFG). In the case of ^{155}Gd Mössbauer quadrupole interactions, the lattice EFG would be dominant in most situations since the Gd^{3+} (4f^7) ion has the higher symmetric valence electron distribution. Thus the e^2qQ value is sensitive to the change of the symmetry and the local structure around the Gd^{3+} ion [1].

The e^2qQ value of **II** is clearly larger than that of **I**. This indicates that the EFG at the Gd site in **II** is larger than that in **I** due to the potassium ions of **II** locating at the position of the zeolitic water molecules of **I**. The distance Gd–K$^+$ is estimated as 4.74 Å, which is the distance between the Gd^{3+} ion and the oxygen atom of zeolitic water in GdFe(CN)$_6$ · 4H$_2$O [4]. The results of e^2qQ indicate that the structures of **I** and **II** can be distinguished easily by ^{155}Gd Mössbauer spectroscopy.

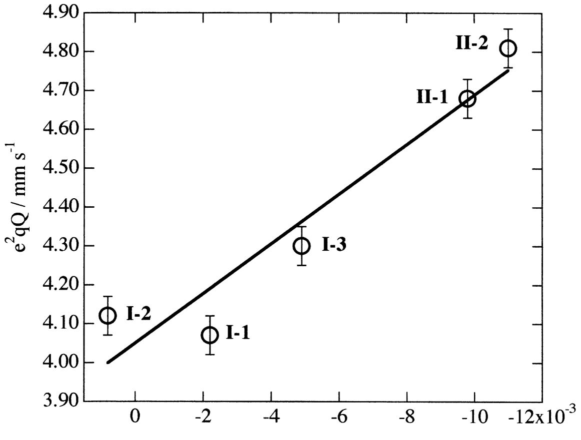

Fig. 3. Plot of e^2qQ versus the orthorhombic distortion, $3^{1/2}a/b-1$ in the crystal structures of GdFe(CN)$_6$ · 4H$_2$O **I-1**, GdCo(CN)$_6$ · 4H$_2$O **I-2**, GdCr(CN)$_6$ · 4H$_2$O **I-3**, KGdFe(CN)$_6$ · 3H$_2$O **II-1** and KGdRu(CN)$_6$ · 3H$_2$O **II-2**.

In the LnM(CN)$_6$ · nH$_2$O and KLnM(CN)$_6$ · nH$_2$O series, the orthorhombic distortion $3^{1/2}a/b-1$ in their crystal structures is often used as parameter to discuss the structural properties of them [3, 5–7]. The a and b are the cell parameters of the orthorhombic Cmcm crystal structure. The hexagonal P6$_3$/m cell can be converted to the orthorhombic Cmcm cell, and the orthorhombic distortion, $3^{1/2}a/b-1$ is zero.

Figure 3 shows a plot of e^2qQ versus the orthorhombic distortion, $3^{1/2}a/b-1$, in their crystal structures. It can be seen that the e^2qQ values increase with increase of the orthorhombic distortion of their crystal structures. The results indicate that the EFG at the Gd site is associated with the orthorhombic distortion, and the symmetry around Gd^{3+} ion becomes lower due to the increase of the large orthorhombic distortion in their crystal structure, which produces the large EFG at the Gd site. The large EFG gives the large value of the e^2qQ. The trend is the same as that for ^{57}Fe Mössbauer data of the LnFe(CN)$_6$ · 4H$_2$O (Ln = Sm ~ Lu) series reported by Katada et al.: the values of the ^{57}Fe Mössbauer Q. S. for the LnFe(CN)$_6$ · 4H$_2$O series increase with increase of the orthorhombic distortion in their crystal structures [13]. Considering the results of

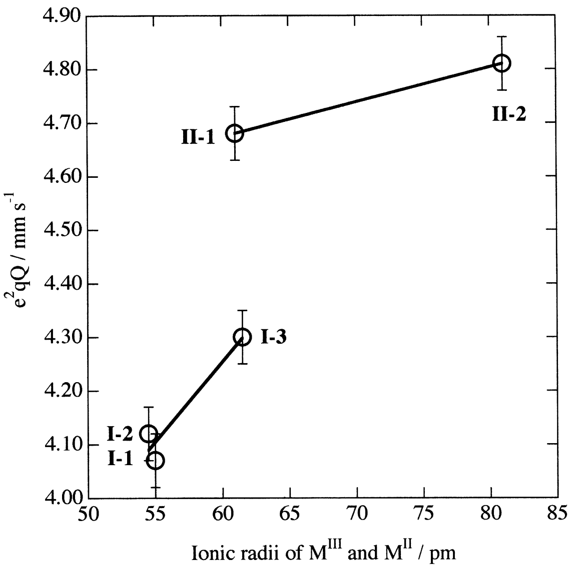

Fig. 4. Plot of e^2qQ versus the ionic radii of the transition metal ions M$^{\mathrm{III}}$ and M$^{\mathrm{II}}$ for the five Gd(III) cyano polymeric complexes: GdFe(CN)$_6$ · 4H$_2$O **I-1**, GdCo(CN)$_6$ · 4H$_2$O **I-2**, GdCr(CN)$_6$ · 4H$_2$O **I-3**, KGdFe(CN)$_6$ · 3H$_2$O **II-1** and KGdRu(CN)$_6$ · 3H$_2$O **II-2**. The six-coordinated low spin ionic radii of M$^{\mathrm{III}}$ and M$^{\mathrm{II}}$ reported by Shannon [20] were used.

their ^{57}Fe and our ^{155}Gd Mössbauer spectroscopy, the degree of the orthorhombic distortion in their crystal structures can influence the octahedron [FeC_6] and the square antiprism [$GdN_6(H_2O)_2$] for $GdM(CN)_6 \cdot 4H_2O$ (M = Cr^{III}, Fe^{III} and Co^{III}) and $KGdM(CN)_6 \cdot 3H_2O$ (M = Fe^{II} and Ru^{II}). The symmetries of the octahedron [FeC_6] and the square antiprism [$GdN_6(H_2O)_2$] can easily be influenced by the surroundings of them, and the results are reflected clearly by their ^{57}Fe and ^{155}Gd Mössbauer spectra. This indicates that ^{155}Gd Mössbauer spectroscopy is a powerful tool for investigating the structural chemistry of the Gd(III) coordination compounds.

Figure 4 shows a plot of e^2qQ versus the ionic radii of M^{III} and M^{II} of six-coordinated low spin states. Evidently e^2qQ increases with increase in the ionic radii of the transition metal ion. The symmetry around the Gd^{3+} ion becomes lower due to the increase in the ionic radii of the transition metal ion through the Gd–NC–M bond. The trend is the same on that of ^{57}Fe Mössbauer Q. S. value versus the ionic radii of Ln for the $LnFe(CN)_6 \cdot nH_2O$ ($n = 5$ for La and Ce, $n = 5$ or 4 for Pr and Nd, $n = 4$ for Sm ~ Lu.) series: the ^{57}Fe Mössbauer Q. S. increases with increase in the ionic radii of the Ln [13].

The orthorhombic distortion in their crystal structures links to the ionic radii of the transition metal ion. The orthorhombic distortion in their crystal structures increases with increase in the ionic radii of the transition metal ion.

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