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Mössbauer Spectroscopy and Magnetization Studies of α- and β-RuCl$_3$

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^{99}Ru Mössbauer spectroscopy and magnetization studies were performed on anhydrous ruthenium trichlorides, black α-RuCl$_3$ and brown β-RuCl$_3$. Measurements on the β-form were made on samples prepared by a new method. The isomers were found to have quite distinct magnetic properties. The ^{99}Ru Mössbauer spectrum of α-RuCl$_3$ exhibits large hyperfine magnetic splitting at 5 K with the magnitude of the hyperfine magnetic field being 209 kOe. This result is consistent with the magnetic susceptibility measurements, which show a sharp cusp, indicating an antiferromagnetic order at $T_N = 15.6 \pm 0.5$ K. The ^{99}Ru Mössbauer spectrum of β-RuCl$_3$ exhibits an electric quadrupole interaction with no hyperfine magnetic interaction. The β-form is thus concluded to be paramagnetic down to 5 K on the basis of the results of the magnetic susceptibility measurements from room temperature to 7 K. The conspicuous difference in the magnetic properties between the two forms is attributable to their crystal structures; i.e., Ru atoms in α-RuCl$_3$ form two-dimensional honeycomb lattices, while those in β-RuCl$_3$ form one-dimensional chains along the *c* direction.

Introduction

The magnetic properties of compounds of 4d transition metals have not yet been thoroughly studied, as compared with those of 3d transition metals. The literature contains contradictory reports, even on basic and simple compounds like anhydrous ruthenium trichlorides. Anhydrous ruthenium trichlorides occur in two forms.[1,2] Fletcher and co-workers reported a series of systematic investigations on the preparation and physical properties of the chlorides.[3–5] From their results of magnetic susceptibility measurements, they concluded that both α- and β-RuCl$_3$ were antiferromagnets with $T_N = 13$ and $\sim$600 K, respectively.[3,5] However, no antiferromagnetic ordering has been detected in either case by neutron diffraction studies.[5]

Mössbauer spectroscopy of ^{99}Ru is an effective technique by which to elucidate the magnetic properties of ruthenium compounds, although the resonant absorption is observed only near or below liquid-helium temperature because the energy of the γ-transition is as high as 89.8 keV (Figure 1).[6] The ^{99}Ru Mössbauer spectra of the β-form reported previously[7,8] presented only a quadrupole splitting, in contradiction to the above interpretation of the results of magnetic measurements. No ^{99}Ru Mössbauer spectrum of the α-form seems to have been reported yet.[9]

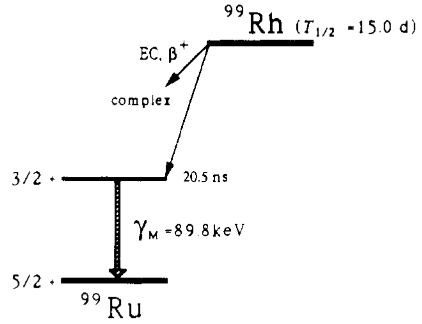

Figure 1. Decay scheme of the source nuclide ^{99}Rh. Only transitions relevant to the Mössbauer study are shown.

The β-form samples used in the previous studies were prepared by heating ruthenium metal in a stream of a chlorine and carbon monoxide mixture at 360–390 °C, which inevitably resulted in contamination of the product by unconverted ruthenium metal and also a byproduct, α-RuCl$_3$. The impurities can have a serious erroneous effect on the measurement of weak magnetization of the β-form.[5]

We developed a new preparative method for β-RuCl$_3$ which afforded a product free of both ruthenium metal and α-RuCl$_3$ and carried out ^{99}Ru Mössbauer spectroscopy and magnetization measurements on both the α- and β-forms of anhydrous ruthenium trichlorides. The results are discussed in terms of their crystal structures and chemical bondings.

Experimental Section

Samples. The sample of α-RuCl$_3$ was obtained from Soekawa Rikagaku Co. and was used with no prior treatment. Its X-ray powder diffraction pattern was in good agreement with that reported by Fletcher et al.[5]

The β-RuCl$_3$ sample was prepared by a new method employing ruthenium carbonyl as the starting material, similar to the preparation of FeCl$_3$ reported by Schäfer and Bayer.[10] The orange powder of triruthenium dodecacarbonyl [Ru$_3$(CO)$_{12}$, manufactured by Strem Chemicals Inc.] was heated for about 3 h at 360 °C in a stream of a mixture of chlorine gas with nitrogen serving as a carrier gas. As was expected, ruthenium carbonyl was found to be superior to ruthenium metal as the starting material with regard to chemical reactivity, beginning

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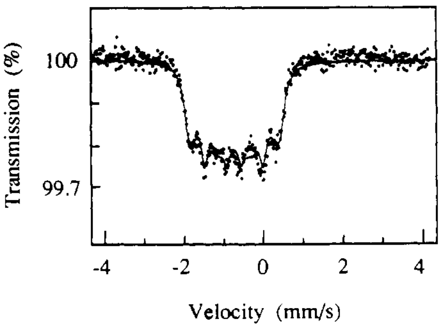

Figure 2. ^{99}Ru Mössbauer spectrum of α-$RuCl_3$ (1.02 g/cm^2) measured at 5 K. The isomer shift is relative to ruthenium metal.

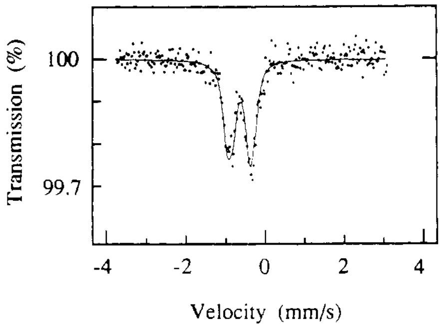

Figure 3. ^{99}Ru Mössbauer spectrum of β-$RuCl_3$ (0.32 g/cm^2) measured at 5 K. The isomer shift is relative to ruthenium metal.

to react above about 100 °C. β-$RuCl_3$ was obtained in the form of a dark brown, fluffy powder on the wall of a Pyrex reaction vessel. The peak positions of X-ray powder diffraction patterns of the product were in good agreement with those reported by Fletcher et al.,[5] though each line was considerably broad owing to low crystallinity.[1] Neither unreacted ruthenium carbonyl nor byproducts, such as α-$RuCl_3$, ruthenium metal, and other carbonyl chlorides, were detected in the pattern. In the thermogravimetric analysis of the product, no appreciable weight loss was detected up to 350 °C, which ensured that the chloride was anhydrous. Scanning electron microscopy showed that the product was dominantly composed of roughly 0.1 (o.d.) × 1 μm rod-type crystals.

Mössbauer and Magnetization Measurements. The Mössbauer source nuclide ^{99}Rh ($T_{1/2}$ = 15.0 d) was produced by the ^{99}Ru(p,n)^{99}Rh reaction[9,11,12] with 12-MeV protons accelerated by the RIKEN 160-cm cyclotron. Metal powder of ^{99}Ru (96.63% enriched) was used as the target, and the irradiated target was used as the Mössbauer source with no prior heat or chemical treatment.

^{99}Ru Mössbauer spectra were obtained using a Mössbauer spectrometer (Ranger, Model MS700M) and a multichannel analyzer (Tracor Northern, Econ-II). Both the source and the absorbers were kept at 5 K in a liquid-helium cryostat during the measurements, and the 89.8-keV Mössbauer γ-rays were detected by a 2-mm-thick NaI(Tl) scintillator. Velocity calibration of the system was done by measuring the Mössbauer absorption lines of ^{57}Fe in an iron foil and in α-Fe_2O_3 against a ^{57}Co/Rh source.

In the present setup with the source, the width (fwhm) and the height of the peak of the ^{99}Ru resonance absorption were 0.25 ± 0.01 mm/s and 1.56 ± 0.05%, respectively, against an absorber of 223 mg/cm^2 natural ruthenium metal.

Magnetic susceptibility measurements were carried out with a vibrating-sample magnetometer (PAR, Model 155) in the temperature range between room temperature and 7 K. The temperature of the samples was measured with a thermocouple of Au(+0.07% Fe) and Ag. The maximum magnetic field applied to the sample was 20 kOe.

Results and Analysis

^{99}Ru Mössbauer spectra obtained on α- and β-$RuCl_3$ at 5 K are shown in Figures 2 and 3, respectively. The spectrum of α-$RuCl_3$ has a partially resolved symmetric hyperfine structure, typically observed in the case of a hyperfine magnetic interaction with no appreciable electric quadrupole interaction. On the other hand, the Mössbauer spectrum of β-$RuCl_3$ consists of an apparent doublet with a small asymmetry, characteristic of an electric quadrupole interaction for ^{99}Ru.

In order to derive the hyperfine parameters for these two chlorides, we analyzed the observed spectra by a least-squares fitting, adopting the following values for electric quadrupole and magnetic dipole moments (denoted Q and μ, respectively) of the ^{99}Ru nucleus: Q_e = 0.22 b and μ_e = -0.285 nm for the nuclear excited state (I_e = $^3/_2$), and Q_g = 0.076 b and μ_g = -0.623 nm for the nuclear ground state (I_g = $^5/_2$).[6] The E2/M1 mixing ratio, δ^2, for the γ-transition was assumed to be 2.7.[11]

The observed spectrum for α-$RuCl_3$ was analyzed with a reasonable χ^2 value assuming a pure magnetic hyperfine interaction. The derived isomer shift (relative to ruthenium metal) and the hyperfine magnetic field are -0.74 mm/s and 209 kOe, respectively. The spectrum for β-$RuCl_3$ was analyzed satisfactorily on the assumption of a pure electric quadrupole interaction with axial symmetry. The derived isomer shift and the quadrupole splitting (defined by $e^2qQ_e/2$) are -0.71 mm/s and -0.75 mm/s, respectively. The Mössbauer parameters of both α- and β-$RuCl_3$ are summarized in Table I together with values quoted from the literature.[7,8]

For both α- and β-$RuCl_3$, the magnetization was found to be proportional to the applied magnetic field up to 20 kOe at all temperatures studied. Therefore, the magnetizations of both chlorides are presented in terms of magnetic susceptibilities throughout this paper.

The temperature dependences of the magnetic susceptibility and its reciprocal for α-$RuCl_3$ are shown in Figure 4. In the high-temperature region above about 120 K, the susceptibility follows the Curie–Weiss law. The effective paramagnetic moment p_{eff} and the paramagnetic Curie temperature Θ were determined to be 2.25 μ_B and 23 K, respectively. The susceptibility has a sharp cusp at about 15 K, suggesting the occurrence of an antiferromagnetic order at this temperature. The susceptibility around this temperature is magnified in the inset of Figure 4. The transition temperature T_N and the molar susceptibility at this temperature are found to be 15.6 ± 0.5 K and 19.0 × 10^{-3} emu/mol, respectively. The transition temperature is slightly higher than that reported by Fletcher et al.,[5] while the maximum value of the susceptibility is in good agreement with theirs.

The temperature dependences of the magnetic susceptibility and its reciprocal for β-$RuCl_3$ are shown in Figure 5. The presence of neither a cusp nor a shoulder at T_N of the α-form certifies that there is no significant contamination of the α-form in the sample. It should be noted that the magnitude of the susceptibility of β-$RuCl_3$ is roughly 1 order smaller than that of α-$RuCl_3$ above T_N of the latter. The susceptibility seems to obey the Curie–Weiss law in the high-temperature region above about 50 K but gradually deviates from the law upon lowering the temperature. In case the law is applicable to the experimental results for the high-temperature region above 50 K, the effective paramagnetic moment and the paramagnetic Curie temperature are tentatively estimated to be 0.9 μ_B and -60 K, respectively. No anomaly suggesting a magnetic transition was observed down to 7 K. The features of the magnetization of β-$RuCl_3$ in the present study are drastically different from those in the previous report.[5] The results of the magnetization measurements for both chlorides in the present study are summarized in Table I along with values quoted from the literature.[3,5]

Discussion

α-$RuCl_3$ is obtained in the form of brilliant black plates by sublimation and is insoluble in both water and ethanol. β-$RuCl_3$ is usually in the form of friable brown powders of relatively low

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Table I. Mössbauer and Magnetic Parameters of α- and β-$RuCl_3$

compd	IS[a] (mm/s)	QS[b] (mm/s)	H_{hf} (kOe)	T_N (K)	p_{eff} (μ_B)	Θ (K)	ref
α-$RuCl_3$	–0.74	~0	209	15.6 ● 0.5	2.25	23	this work
				13	~2.2	32–40	3, 5
β-$RuCl_3$	–0.71	–0.75	0	*c*	0.90	–60	this work
	–0.714	0.85					7
	–0.642	+0.69					8
				≈600			5

[a] Isomer shift relative to ruthenium metal. [b] Quadrupole splitting defined by $e^2qQ_e/2$, where Q_e is the electric quadrupole moment of the ^{99}Ru nuclei in the excited state. [c] Paramagnetic down to 5 K.

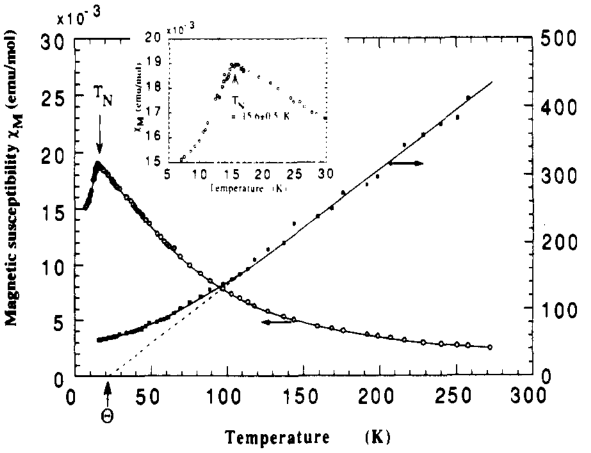

Figure 4. Temperature dependences of the magnetic susceptibility and its reciprocal for α-$RuCl_3$. The inset presents the susceptibility around the Néel temperature.

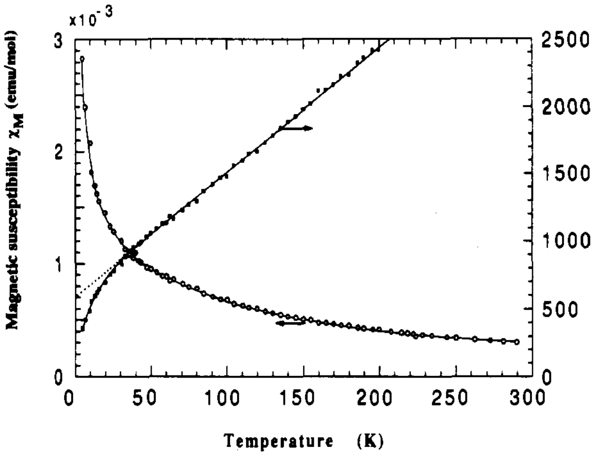

Figure 5. Temperature dependences of the magnetic susceptibility and its reciprocal for β-$RuCl_3$.

crystallinity and is soluble in ethanol. Irreversible transformation from β-$RuCl_3$ to α-$RuCl_3$ occurs at 450 °C.[2,13]

In α-$RuCl_3$, Ru(III) atoms form a honeycomb-lattice layer positioned between triangular-lattice layers of Cl^- ions (see Figure 6).[5] The units of the sandwich layers are stacked so as to make the Cl^- ions form fcc-type close packing. The bonding between adjacent Cl^- layers having no Ru(III) atoms between them is of the van der Waals type and is expected to be very weak. Chloride ions of β-$RuCl_3$ form the hexagonal close-packed structure. Ruthenium(III) atoms occupy one-third of the octahedral interstices between Cl^- layers and form chains along the *c* axis perpendicular to the layers (see Figure 7).[5]

The Mössbauer effect of ^{99}Ru on the γ-transition is observed between the ground and the 89.8-keV levels of the nuclei (Figure 1). The spins of the levels are $I_e = {}^3/_2$ and $I_g = {}^5/_2$, respectively. The transition is a mixture of magnetic dipole and electric quadrupole interactions with an E2/M1 mixing ratio of 2.7. The dependence of the isomer shift for ^{99}Ru on the chemical valence state shows a similarity to that for ^{57}Fe, though the sign is reversed because of the positive value of $\Delta R/R$ for ^{99}Ru. The observed values of the isomer shift for α- and β-$RuCl_3$ (–0.74 and –0.71 mm/s, respectively) are in the range typical for trivalent ruthenium compounds, in which Ru(III) atoms are all in the low-spin state.[14,15] When the nuclei of ^{99}Ru are in a magnetic field with no electric field gradient, 18 absorption lines appear symmetrically in the Mössbauer spectrum as a result of the mixed transitions

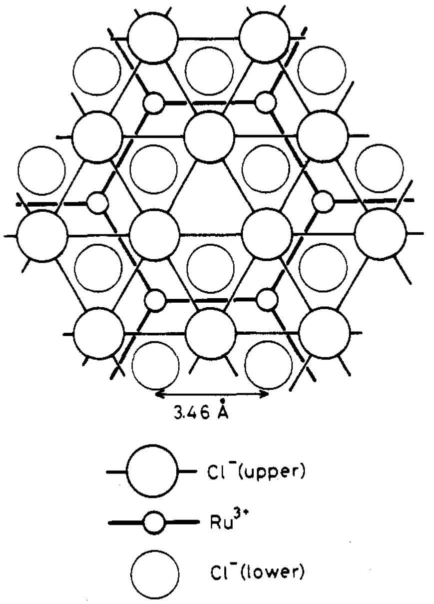

Figure 6. Crystal structure of α-$RuCl_3$. The direction of the *c* axis is perpendicular to the "honeycomb" lattices.

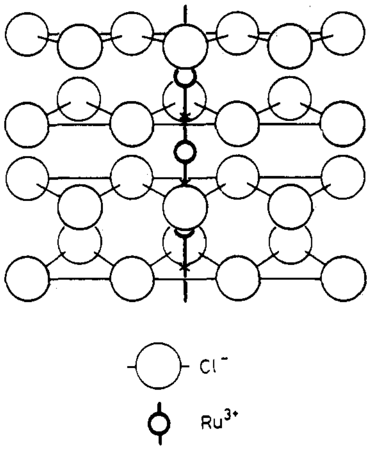

Figure 7. Crystal structure of β-$RuCl_3$. The Ru(III) atoms occupy one-third of the octahedral interstices.

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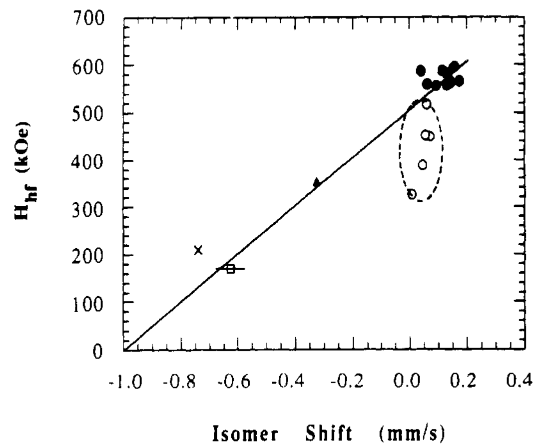

Figure 8. Relation between the isomer shifts and the hyperfine magnetic fields of α-RuCl$_3$ and magnetic ruthenium oxides at liquid-helium temperature: ●, Ru(V) oxides with the perovskite structure;[16,17] ○, Ru(V) oxides with the hexagonal structure related to barium titanate;[18] ▲, a Ru(IV) oxide with the perovskite structure (SrRuO$_3$);[19] □, a Ru(III) oxide (estimated);[20,21] ×, α-RuCl$_3$ (present work).

between the Zeeman-split nuclear levels. An asymmetric doublet, each branch consisting of three unresolved lines, appears in the presence of an electric field gradient of ordinary magnitude.

By the present Mössbauer study, it has been clarified that the magnetic properties of α- and β-RuCl$_3$ are quite different. For α-RuCl$_3$, the ^{99}Ru Mössbauer spectrum at 5 K exhibits hyperfine magnetic splitting, indicating an antiferromagnetic order at this temperature. This is consistent with the observed magnetic susceptibility, which shows a sharp cusp at 15.6 K. On the other hand, the magnetic susceptibility of β-RuCl$_3$ is roughly 1 order smaller than that of α-RuCl$_3$ and exhibits no anomaly, which indicates a magnetic ordering down to 7 K. The ^{99}Ru Mössbauer spectrum for β-RuCl$_3$ shows no magnetic splitting at 5 K, and an appreciable electric quadrupole splitting is observed instead. The marked contrast of the magnetic properties of these two chlorides is discussed in terms of the characteristic crystal structures of these two compounds, which have the same chemical composition.

The α-Form. α-RuCl$_3$ is the first compound containing only Ru(III) atoms for which the hyperfine magnetic field has been determined by ^{99}Ru Mössbauer spectroscopy. Figure 8 is a diagram illustrating the isomer shift (abscissa) and the hyperfine magnetic field of ^{99}Ru (ordinate) in α-RuCl$_3$, together with those of octahedral sites in various magnetic ruthenium oxides at liquid-helium temperature.[16-21] The points surrounded by the dashed line represent compounds with a hexagonal structure related to barium titanate, in which two RuO$_6$ octahedra form a dimer, sharing their faces.[18] The remaining oxides have the perovskite structure, in which RuO$_6$ octahedra share their corners. The value estimated by Greatrex and co-workers for Ru(III) atoms in magnetically ordered oxides[16,20,21] is also indicated in the diagram. The group of points around IS = 0.1 mm/s represent Ru(V) atoms in oxides,[16,17] and the point at IS = −0.3 mm/s denotes Ru(IV) atoms in SrRuO$_3$.[19] It can be seen from the diagram that the isomer shifts for penta-, tetra-, and trivalent ions are almost equidistantly separated. This fact indicates that the effect of 4d electrons on the s-electron density at ^{99}Ru is almost linear relative to the number of 4d electrons of the Ru atom.

In the present discussion on the hyperfine magnetic fields at ^{99}Ru, we omit the oxides with the hexagonal structure related to barium titanate because their magnetic properties are quite different from the others owing to their dimer structure. With the exception of the points for these oxides, all points in the diagram are in a virtually straight line; i.e., the magnitude of the hyperfine magnetic field is linearly related to the value of the isomer shift, a measure of the valence state of Ru atoms. Moreover, it can be said that the hyperfine magnetic field is almost proportional to the number of unpaired 4d electrons of Ru atoms if we assume that they are all in low-spin states in these compounds. This finding shows that the hyperfine magnetic fields at ^{99}Ru, which arise from the polarization of s electrons at ^{99}Ru, are caused mainly by the unpaired spins of the ^{99}Ru 4d electrons and that their contribution to the hyperfine magnetic field is additive. This finding is circumstantial evidence that Ru(III), Ru(IV), and Ru(V) atoms of the compounds are all in low-spin states. The magnitude of the hyperfine magnetic field at ^{99}Ru is estimated to be about 200 kOe per unpaired 4d electron, which should be compared with 110 kOe for 3d transition metal elements in oxides.[22]

In the above discussion, we neglected the factors dependent on ligand anions, i.e., oxide and chloride. The effect of the factors is considered to be small because the covalencies in chlorides are known to be comparable to those in oxides.[23]

The absence of appreciable electric quadrupole interactions at ^{99}Ru nuclei in α-RuCl$_3$ indicates that the octahedral configuration of ligand Cl$^-$ ions around them is highly symmetric and, moreover, that their valence electrons are distributed with nearly cubic symmetry. This situation for α-RuCl$_3$ is quite similar to that for ^{57}Fe in isomorphous FeCl$_3$[24] and forms a striking contrast to the case of the β-form discussed below.

The value of the effective paramagnetic moment, $p_{eff} = 2.25$ μ_B, derived from the result of magnetization measurements on α-RuCl$_3$, is considerably larger than the spin-only value of 1.73 μ_B for the low-spin state ($S = {}^1/_2$) of Ru(III). However, such larger values are common for Ru(III) atoms in octahedral sites of many complexes,[2,25] for which the discrepancy from the spin-only value has been explained by the contribution of the orbital angular momentum of a hole in the t_{2g} orbitals of 4d electrons.[25]

Although the magnetically ordered state of α-RuCl$_3$ at low temperatures below T_N = 15.6 K is antiferromagnetic, the paramagnetic Curie temperature is positive (Θ = 23 K), meaning that the exchange interactions between Ru(III) atoms are ferromagnetic on the average. This magnetic property can be explained in relation to the layered crystal structure of α-RuCl$_3$. Adjacent Ru(III) atoms in the same layer can interact strongly via the Cl$^-$ ions in the neighboring layers, but the interlayer magnetic interaction is considered to be a subsidiary one in the whole magnetic structure because Ru(III) atoms can interact with those in the next layers only through two Cl$^-$ layers. It is reasonably expected from the positive sign of the paramagnetic Curie temperature that the intralayer magnetic interaction is ferromagnetic. Thus, the most probable magnetic structure at low temperatures is the antiferromagnetic order of the ferromagnetic Ru(III) atom layers, as was suggested in ref 5. The large value of Θ as compared with T_N shows that the predominant interactions for the magnetic ordering are the intralayer ferromagnetic ones and the weak interlayer interactions only assist

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the three-dimensional ordering. In a fairly wide temperature range of the paramagnetic region, i.e., between T_N and about 100 K (about 6 times as large as T_N), a deviation from the Curie–Weiss law is observed. This phenomenon can be understood by considering the growth of short-range ferromagnetic order within the Ru layers on lowering of the temperature.

The β-Form. Our ^{99}Ru Mössbauer spectrum for β-$RuCl_3$ is free of magnetic splitting, as are the previous ones,[7,8] which obviously denies any magnetically ordered state down to 5 K. The magnitudes of the splittings of the apparent doublets in the spectra are almost the same, but the asymmetry of the doublet in the present study appears to be the reverse of those in the previous ones. According to our result, the sign of the electric field gradient ($-|e|q$) is derived as positive. The origin of the electric field gradient is discussed below.

Fletcher et al. reported that the magnetic susceptibility of β-$RuCl_3$ decreased with a decrease in temperature below 300 K and had a minimum at ~150 K. After allowing for the contribution of contaminating α-$RuCl_3$ as well as that of diamagnetic and temperature-independent terms, they concluded that β-$RuCl_3$ was antiferromagnetic below about 600 K. With the theory of linear Heisenberg chains,[26] they deduced an exchange interaction J as large as ~−800 K.[5] The results of magnetization measurements on our β-$RuCl_3$ sample, free of both the α-form and ruthenium metal, were wholly distinct from theirs.[3-5] The observed magnetic susceptibility is much smaller than that of α-$RuCl_3$ and exhibits no anomaly in the temperature range studied. Thus, β-$RuCl_3$ is concluded to be paramagnetic between 7 and 300 K on the basis of the present results. This conclusion is consistent with the results of ^{99}Ru Mössbauer spectroscopy described above.

From the crystallographic point of view, the magnetic interaction between Ru(III) atoms in the same layer of β-$RuCl_3$ is considered to be very weak because the distance between them is large. On the other hand, the Ru(III) atoms are expected to have an appreciable magnetic interaction within the chain along the c axis through the intervening Cl^- ions.

Supposing that Ru(III) atoms in β-$RuCl_3$ possess a localized magnetic moment of 4d electrons as in α-$RuCl_3$, the effective paramagnetic moment, 0.9 μ_B, obtained from the $1/\chi$–T curve (Figure 5), is thought to be too small, while the absolute value of the paramagnetic Curie temperature, −60 K, is considered too large. The most plausible interpretation of the observed small susceptibility is that the 4d electrons in t_{2g} orbitals of the Ru(III) atoms in β-$RuCl_3$ are strongly delocalized in the chain along the c axis, losing their localized character. They act as itinerant electrons for which the Curie–Weiss law is not applicable, so that the Curie constant and the Curie temperature described above are only apparent values and are not to be compared with those of α-$RuCl_3$. Since 4d electrons delocalized one-dimensionally can bring about a large electric field gradient, the above explanation is qualitatively consistent with the results of the Mössbauer measurements. The absence of such a delocalization in α-$RuCl_3$ is thought to result in a lack of appreciable electric quadrupole interactions. Another postulated reason for quenching of the magnetic moment is that the Ru(III) atoms form a dimer. The peaks of (00l) with l = odd would be detected in the X-ray diffraction pattern if such a dimer was formed, but for the present β-$RuCl_3$ samples, no such peaks were confirmed.

Conclusion

The results of the ^{99}Ru Mössbauer spectroscopy and the magnetic susceptibility measurements on α-$RuCl_3$ clarify the antiferromagnetic order of Ru(III) atoms below $T_N = 15.6 \pm 0.5$ K. The magnitude of the hyperfine magnetic field at 5 K is 209 kOe. The chloride is the first compound containing only trivalent Ru atoms for which the magnetic field has been determined. From the results of the present study, together with those in the literature, a linear relationship is established between the isomer shifts and the number of 4d electrons of Ru(III), Ru(IV), and Ru(V) atoms in chlorides and oxides. It is also found that the hyperfine magnetic fields at ^{99}Ru nuclei are proportional to the number of unpaired 4d electrons, with a magnitude of approximately 200 kOe per unpaired electron. The paramagnetic Curie temperature shows that the interactions between the Ru(III) atoms within the same layer are ferromagnetic, while those between the adjacent layers are antiferromagnetic.

Ruthenium carbonyl is superior to ruthenium metal as the starting material for the preparation of β-$RuCl_3$, affording samples free of both metal and the α-form. The β-form thus prepared shows no hyperfine magnetic interaction in the Mössbauer spectrum at 5 K, definitely indicating that it is not magnetically ordered down to this temperature. This conclusion is supported by the magnetic susceptibility, which follows the Curie–Weiss law down to about 50 K. The effective paramagnetic moment, $p_{eff} = 0.9\ \mu_B$, is much smaller than those of other Ru(III) compounds. This is ascribed to delocalization of 4d electrons in the t_{2g} orbitals along the chain in the direction of the c axis. This interpretation is consistent with the appreciable electric field gradient observed in the Mössbauer spectrum.

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