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Deuteron Magnetic Resonance Study in $Co(ND_3)_6Cl_3$

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Deuteron quadrupole coupling tensors in $Co(ND_3)_6Cl_3$ were determined at various temperatures. The observed quadrupole coupling shows that $Co(ND_3)_6{}^{3+}$ ions execute a rapid isotropic reorientation at high temperatures (above 320°K for one of the sites (the 4f sites) and above 190°K for another (the 2e sites)), while at low temperatures (below 190°K for the 4f sites, and 170°K for the 2e sites), only a C_3 axis reorientation of the ligand ND_3 groups is present. The deuteron resonance spectra clearly show that $Co(ND_3)_6{}^{3+}$ ions in the 4f sites begin to reorient about one of the three C_4 axes at intermediate temperatures (about 240°K). On the basis of the orientation of quadrupole tensors, probable orientations of $Co(ND_3)_6{}^{3+}$ ions in the 4f sites in the crystal are proposed. Additional measurements of the proton resonance on a single crystal of $Co(NH_3)_6Cl_3$ support the results obtained from the deuteron resonance. To obtain the reorientation rates and the activation energies of these reorientational motions, the deuteron resonance line width at the 4f sites is measured at various temperatures and at various crystal orientations. From the temperature dependence of the line width, the presence of two cations with slightly different rates at the 4f sites is suggested. However, because of the limits set by the various experimental conditions, reliable values of the reorientation rates and activation energies could not be obtained.

Structure and molecular motions in the hexamminecobalt(III) chloride crystal have been studied by several authors by measurements of the line shape and of the second moment of the proton magnetic resonance. Murray and Waugh[1] investigated the $Co(NH_3)_6X_3$-type compounds and found that the protons of the NH_3 ligand reorient about its C_3 axis at the temperature of liquid nitrogen. They also found that these complex salts show unusual and very broad line-width transitions in the cases of X=Cl, Br, I, and NO_3. They explained these phenomena in terms of over-all reorientations of complex cations occupying two nonequivalent crystal sites. Dharmatti, Saraswati, and Vijayaraghavan[2] confirmed the existence of two kinds of crystal sites in cobalt atoms by observing the ^{59}Co NMR line, which splits into two components at a static magnetic field of 3 k gauss. Kim[3] measured the proton second moment of $Co(NH_3)_6Cl_3$ at very low temperatures and showed that the reorientation of ammonia molecules about their C_3 axes does not freeze, even at the temperature of liquid helium. In order to obtain detailed information about the structure and motions in this crystal, we measured the deuteron magnetic resonance on single crystals of deuterated hexamminecobalt(III) chloride.

In a nucleus with a nuclear spin greater than 1/2, the NMR spectrum exhibits quadrupole splitting, which is often strongly affected by nuclear motions. It is well known that if two nuclei at different sites exchange positions at a rate much greater than the separation between the lines of the two sites, the field gradient at the nucleus is averaged and the absorption line is observed at the averaged position of the two lines.[4]

In the present case, the field gradient of the deuteron is averaged by the C_3 axis reorientation of ND_3 in a $Co(ND_3)_6{}^{3+}$ ion because this motion is sufficiently rapid. Assuming an axially symmetric field gradient in the direction of the N–D bond, the direction of the maximum principal component of the averaged field gradient, q_{zz}, can be assumed to be parallel to the Co–N bond direction. Since the $Co(ND_3)_6{}^{3+}$ ion possesses an approximate O_h symmetry, three types of over-all reorientational motions may be considered——the reorientations about three C_4 axes, those about four C_3 axes, and those about six C_2 axes. If the reorientation about one of the C_4 or C_2 axes is sufficiently rapid, two

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[1] G. R. Murray, Jr., and J. S. Waugh, *J. Chem. Phys.*, **29**, 207(1958).

[2] S. S. Dharmatti, V. Saraswati and R. Vijayaraghavan, *Proc. Colloque Ampere*, **13**, 133 (1960).

[3] P. H. Kim, *J. Phys. Soc. Japan*, **15**, 445 (1960).

[4] A. Abragam, "The Principles of Nuclear Magnetism," Oxford Clarendon Press, Oxford (1961), Ch. 10.

of the three axially-symmetric q-tensors in the three N–Co–N directions average to a new axially-symmetric q-tensor, one which has $-(1/2)$ the original value and which is parallel to the third. On the other hand, if the reorientation about any one of the C_3 axes is rapid, the field gradient becomes nearly zero. If the reorientations about various axes occur simultaneously (isotropic reorientation), so that all the six ligand molecules can exchange their positions, the field gradient also becomes nearly zero. Therefore, by deuteron resonance study, we can expect to find out what type of motion is present in the crystal.

Experimental

The sample was prepared by the usual method.[5] Deuteration was easily performed by the successive isotope exchange of $Co(NH_3)_6Cl_3$ with D_2O. A single crystal was obtained by slowly cooling a saturated heavy-water solution. The over-all dimensions of a typical sample used in the present experiment are about $10 \times 7 \times 7\ mm^3$. The measurements were carried out at 10 Mc/sec using a Robinson-type detector. The output signal of the spectrometer was amplified by a narrow-band 'lock-in' amplifier, and the derivative of the absorption line was recorded. Temperature control was accomplished by using an electric heater wound outside the probe or by passing through cooled nitrogen gas obtained by boiling liquid nitrogen. Temperature control within ±1°C was attained by this method. For the deuteron, the nuclear spin $I=1$; therefore, the quadrupole interaction gives a pair of lines ($m=1\leftrightarrow 0$ and $0\leftrightarrow -1$). In order to eliminate the second-order effect of quadrupole interaction and the error due to field drift, the frequency separation between the pair of lines ($2\Delta\nu$) was measured instead of the separation of each sideband from the Larmor frequency. The angular dependence of the quadrupole splitting is given by:

$$2\Delta\mu = \frac{3}{4h}e^2Q\left\{-q_{zz} + (q_{xx}-q_{yy})\cos 2\theta_z + 2q_{xy}\sin 2\theta_z\right\} \quad (1)$$

where q_{ij} is the ij element of the field gradient tensor, where x, y, and z are the coordinates fixed to the probe head, z being along the axis of rotation, and where θ_z is the angle of rotation of H_0 measured from the x axis. From the measurements of rotation patterns about three mutually orthogonal axes, all the components of the p-tensor can be determined.[6] Since the crystal structure of $Co(NH_3)_6Cl_3$ is monoclinic ($\beta=91°19'$),[7] we measured the rotation patterns about the b axis, c axis, and the a* axis (perpendicular to the b and c axes).

Results

The observed spectra are strongly dependent on the temperature. At 320°K, a single broad line at the Larmor frequency (denoted by line 1) and a pair of sharp lines with a separation of several gauss (lines 2) are observed. The intensity of line 1 decreases as the temperature is lowered,

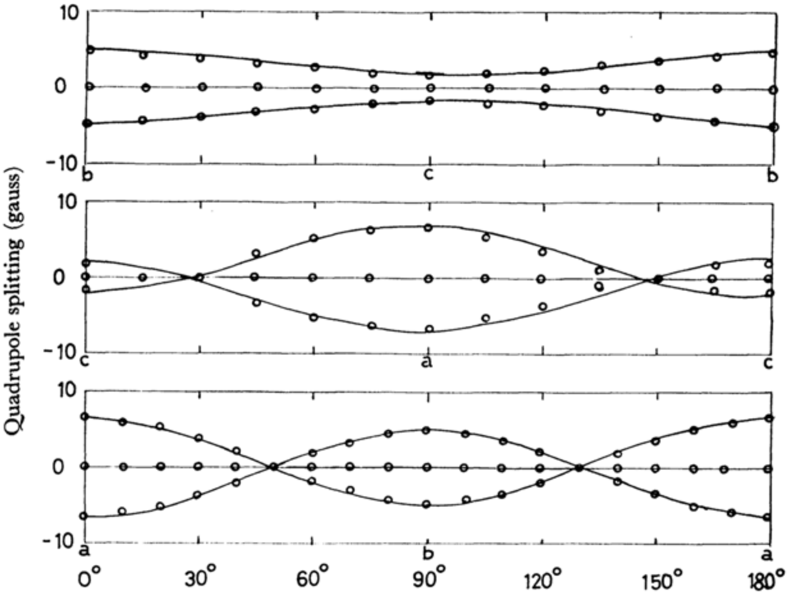

Fig. 1. Rotation pattern of deuteron resonance in $Co(ND_3)_6Cl_3$ at 320°K.

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[5] K. Yamasaki, "Zikken Kagaku Koza," Vol. 11, Maruzen, Tokyo (1958), p. 18.

[6] G. M. Volkoff, H. D. Petch and D. W. Smellie, *Can. J. Phys.*, **30**, 270 (1952).

[7] P. Groth, "Chemische Kristallographie," Teil 1, Engelman, Leipzig (1906).

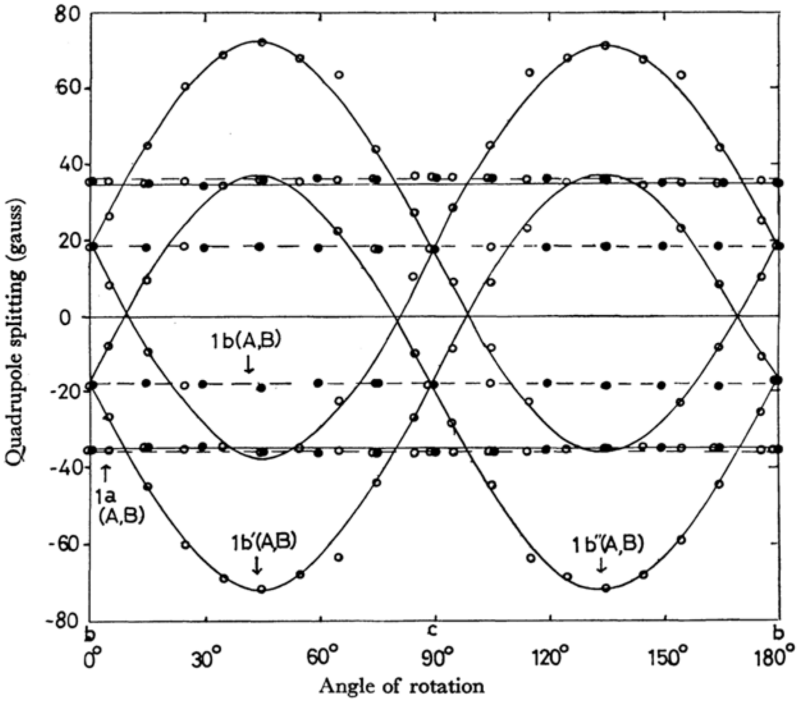

Fig. 2. a*Axis rotation pattern of deuteron resonance in $Co(ND_3)_6Cl_3$.
● at 240°K. ○ at 190°K.
In this pattern the lines due to the ions A and B defined in Fig. 6 overlap each other.

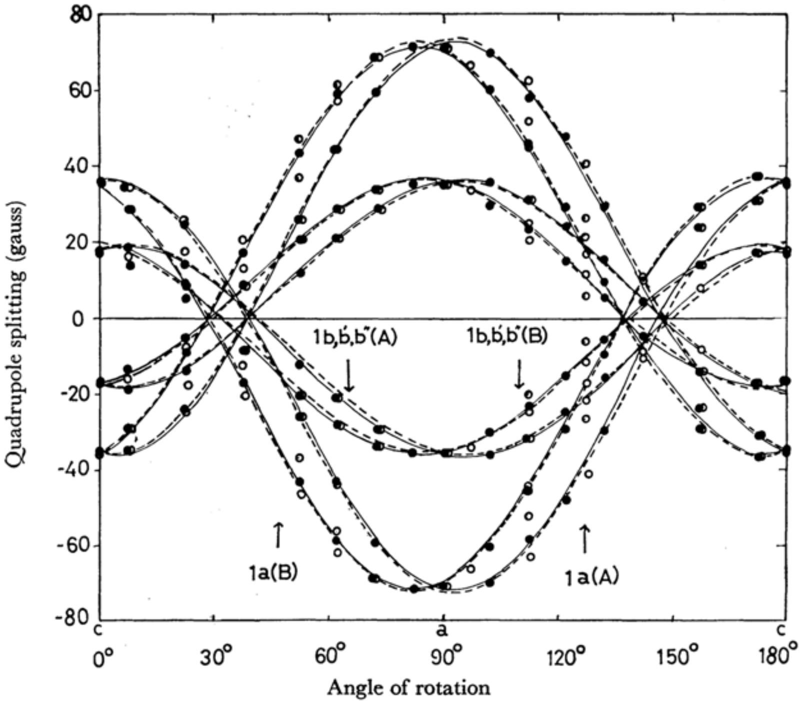

Fig. 3. b Axis rotation pattern of deuteron resoance in $Co(ND_3)_6Cl_3$
● at 240°K, ○ at 190°K.
In this pattern, the lines due to the ions A and B defined in Fig. 6 are separately observed, but the lines 1b′ and 1b″ overlap each other.

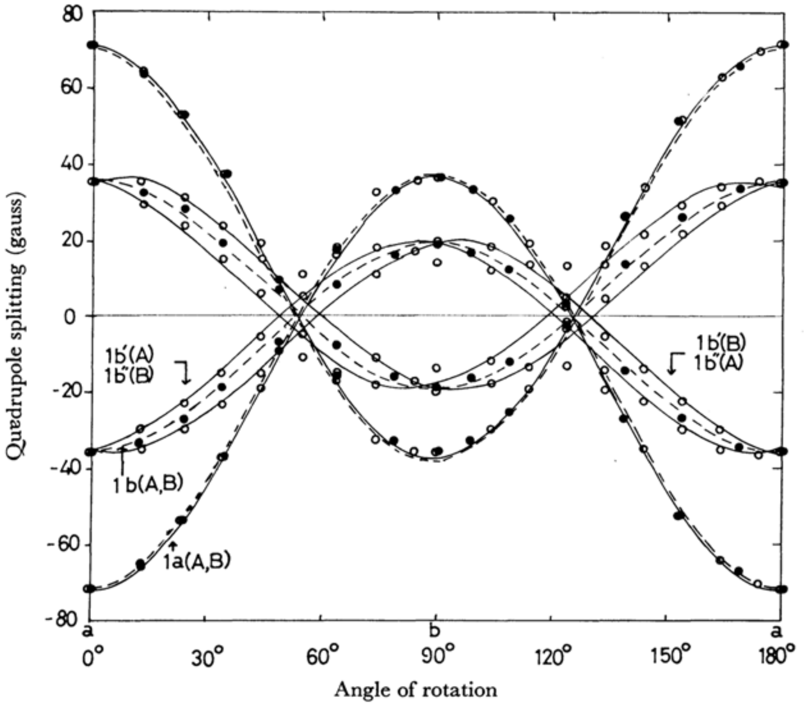

Fig. 4. c Axis rotation pattern of deuteron resonance in $Co(ND_3)_6Cl_3$.
● at 240°K, ○ at 190°K.
In this pattern, the lines 1b′ (A) and 1b″ (B) or 1b″ (A) and 1b′ (B) overlap each other.

until it almost fades out at 305°K. New weak lines begin to appear at this temperature. These lines are clearly distinguished as pairs of lines (1a and 1b) at 240°K. At 190°K, the line 1b further splits into two lines (1b′ and 1b″). The lines 2 become weak as the temperature is lowered and almost fade out at 170°K. Eight or nine pairs of lines are observed at the temperature of liquid nitrogen.

a) Lines 1 and 2. The spectrum at 320°K consists of lines 1 and 2. The rotation patterns are shown in Fig. 1. Line 1 has no angular dependence, but at a particular angle a small splitting is observed when the modulation width is decreased. The analysis of the two rotation patterns, 1 and 2 gives $e^2qQ/h \approx 0$ for line 1 and $e^2qQ/h = 5.6 \pm 0.5$ kc/sec, $\eta = 0.45$ for line 2. The principal axes, z, y, and x, of the field gradient tensor of the deuteron for line 2 are nearly parallel to the a, b, and c axes respectively. The spectrum at room temperature consists of lines 2 and lines 1a and 1b. Lines 1a and 1b are broad and weak. The lines 2 at room temperature are identical to that at 320°K within the limits of experimental error.

b) Lines 1a, 1b, 1b′, and 1b″. At 240°K, the lines 1a and 1b are observed in addition to the lines 2. In the b axis rotation pattern, the lines 1a and 1b consist of four pairs of lines (1a(A), 1a(B), 1b(A), and 1b(B)), while in the c axis and the a* axis rotation patterns these lines consist of two pairs ([1a(A), 1a(B)] and [1b(A), 1b(B)]).[*1] The rotation patterns at 240°K are shown in Figs. 2, 3, and 4 by solid circles.

At 190°K, the lines 1b split into 1b′ and 1b″ but 1a remains unchanged. In the a* axis rotation pattern, the spectra consist of three pairs of lines ([1a(A), 1a(B)], [1b′(A), 1b′(B)], and [1b″(A), 1b″(B)]). In the b axis rotation pattern, the spectra consist of four pairs (1a(A), 1a(B), [1b′(A), 1b″(A)], and [1b′(B), 1b″(B)]). In the c axis rotation pattern, the spectra consist of three pairs ([1a(A), 1a(B)], [1b′(A), 1b″(B)], and [1b″(A), 1b′(B)]). The rotation patterns at this temperature are shown in Figs. 2, 3, and 4 by open circles. In Figs. 2, 3, and 4, the lines 2 are omitted because they are almost identical to those at 320°K. The field gradient tensors derived from the analysis of the rotation patterns at 240°K and 190°K are shown in Table 1. The quadrupole coupling constants corresponding to the lines 1a(A), 1a(B), 1b′(A), 1b′(B), 1b″(A), and 1b″(B) are the same (about 63 kc/sec) within the limits of experimental error. Similarly, the coupling constants corresponding to the lines 1b(A) and 1b(B) are nearly the same

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[*1] [1a(A), 1a(B)] signifies that lines 1a(A) and 1a(B) are observed as a single line because they approximately overlap.

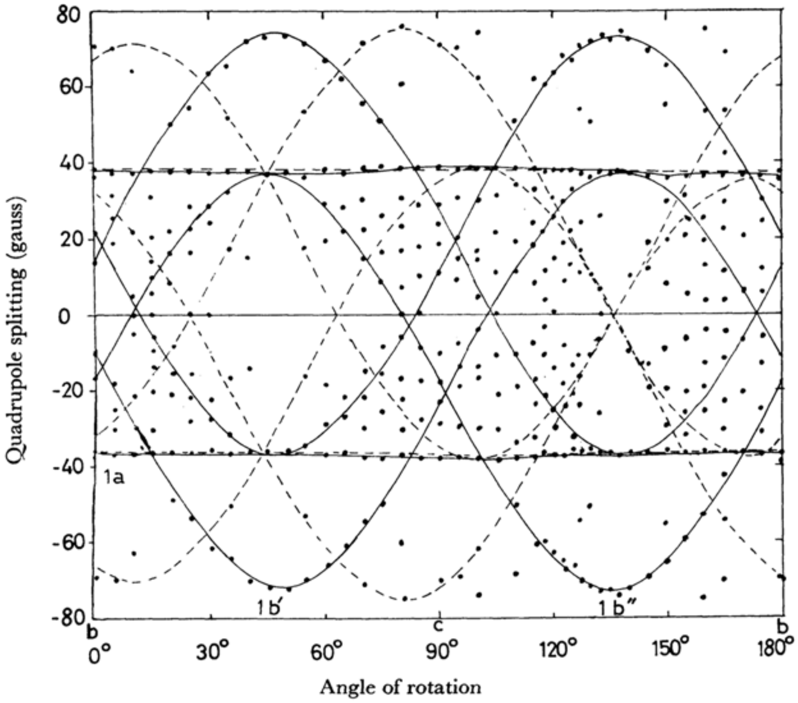

Fig. 5. a* Axis rotation pattern of deuteron resonance in $Co(ND_3)_6Cl_3$ at 77°K.

Table 1. Observed deuteron quadrupole interactions in $Co(ND_3)_6Cl_3$

Temperature	240°K					
Absorption line	1a A	1a B	1b A	1b B		
e^2qQ/h (±1 kc)	62.7	63.6	32.2	32.6		
η (±0.05)	0.02	0.01	0.02	0.02		
Direction of q_{zz} axis* (±3°) θ	3°	7°	3°	7°		
Direction of q_{zz} axis* (±3°) φ	180°	0°	180°	0°		
Temperature	190°K					
Absorption line	1a A	1a B	1b′ A	1b′ B	1b″ A	1b″ B
e^2qQ/h (±1 kc)	62.7	63.0	64.0	63.8	63.5	63.5
η (±0.05)	0.04	0.00	0.02	0.03	0.00	0.05
Direction of q_{zz} axis* (±3°) θ	3°	4°	86°	93°	94°	86°
Direction of q_{zz} axis* (±3°) φ	180°	0°	45°	45°	−45°	−45°

* θ is the polar angle with respect to the a* axis.
ϕ is the azimuthal angle measured from the b axis.

(about 32 kc/sec). The latter value is approximately one half the former value. The asymmetry parameter, η, is nearly zero in all cases.

c) Spectra at the Temperature of Liquid Nitrogen. The spectra at the temperature of liquid nitrogen are very complicated. Although the lines 1a, 1b′, and 1b″ are still recognizable, many other lines appear over the range of about 150 gauss. Therefore, it is almost impossible to get each curve of the rotation pattern separately. The a* axis rotation pattern is shown in Fig. 5 as an example.

Discussion

Waugh and Murray[1)] reported that the crystal structure of the hexamminecobalt(III) chloride is monoclinic, containing three cobalt atoms in a unit cell, and that these three atoms are at two different crystallographic sites in a relative abundance of 2 : 1. However, Giménez-Hugget[8)] recently reported that the space group for this compound is $P2_1/m$ and that a unit cell contains twelve cobalt atoms at two 4f sites and two 2e sites. He also concluded that the nitrogen atoms of four NH_3 groups lie on a (010) plane and that of the other two NH_3 groups, one lies above and one below this plane. The integrated intensity ratio of lines 1 and 2 at 320°K at the angle of maximum separation is approximately 2 : 1. Therefore, the lines 1 and 2 are assigned to the signals from the ions at the 4f and 2e sites respectively. The temperatures at which these lines disappear (260—320°K for the lines 1, and 170—190°K for the lines 2) are in good agreement with the proton line-width transition temperatures, 260—330°K and 150—230°K respectively.[1)] Since the quadrupole splittings of the lines 1 and 2 are both very small, it is confirmed that a rapid isotropic reorientation

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8) M. Giménez-Hugnet, *Dissertation Abstr.*, **22**, 2209 (1962), Thesis, Purdue Univ. (1961).

occurs in the complex cations at both sites above room temperature. The small quadrupole coupling may be due to the distortion of a $Co(ND_3)_6^{3+}$ ion from the O_h symmetry and the effect of the external crystal field, a situation similar to that in the case of the rapidly reorienting ND_4^+ ion in some ammonium salts.

Lines 1a, 1b, 1b′, and 1b″ seem to originate from the complex cations belonging to the 4f sites, because on cooling they appear after line 1 has faded out. On the basis of knowledge obtained from proton resonance studies, NH_3 ligands can be said to reorient rapidly about their C_3 axes throughout the temperature range of our experiment. Therefore, at 190°K, the maximum principal axis of the field gradient tensor of the deuteron is found to be approximately parallel to the Co–N bond direction by motional averaging. If the D–N–D angles of a coordinated ammonia molecule are tetrahedral, the motionally-averaged deuteron quadrupole coupling constant will be one-third that of the rigid molecule, assuming an axially symmetric field gradient in the direction of the N–D bond. From the known deuteron quadrupole coupling constants for the rigid ND_4^+ ion[9,10] (179.9 kc/sec, 180.0 kc/sec, and 174 kc/sec in ND_4Cl, ND_4Br, and $(ND_4)_2SO_4$ respectively), the quadrupole coupling averaged by the C_3 axis reorientation of ND_3 can be estimated to be about 60 kc/sec. This is in good agreement with the observed quadrupole coupling constants in $Co(ND_3)_6Cl_3$ at 190°K, about 63 kc/sec. Therefore, the lines 1a, 1b′, and 1b″ at 190°K are assigned to signals from ND_3 groups of the three different Co–N bond directions of a $Co(ND_3)_6^{3+}$ ion. The fact that absorption lines due to ND_3 groups corresponding to three Co–N bond directions are separately observed indicates that the complex cations at 4f sites are stationary at 190°K. From the directions of the field gradient tensors, the following conclusions concerning the orientations of $Co(ND_3)_6^{3+}$ ions at the 4f sites can be reached: (1) $Co(ND_3)_6^{3+}$ ions at the 4f sites have two different orientations, shown as A and B in Fig. 6 (A and B each seem to correspond to one of the two 4f sites). (2) One of the Co–N bond directions in a $Co(ND_3)_6^{3+}$ ion (1–2 in Fig. 6) is about 5° away from the a* axis on the a*c plane, while the other two Co–N bond directions (3–4 and 5–6) make angles of about 45° with the b axis, where deuterons at 1 and 2 give lines 1a, deuterons at 3 and 4 give lines 1b′, and deuterons at 5 and 6 give lines 1b″. These conclusions are not in accord with Giménez-Hugget's findings that four NH_3 are here placed in a (010) plane and that all $Co(NH_3)_6^{3+}$ ions have the same orientation. However, since the deuteron resonance spectra clearly show more than one orientation of $Co(ND_3)_6^{3+}$ ions, his conclusion concerning the nitrogen positions does not seem to be correct.

At 240°K, the lines 1b appear at the averaged positions of the lines 1b′ and 1b″, which have already faded out by this temperature, while the lines 1a remain the same as those at 190°K. This can be explained by a uniaxial reorientation of the $Co(ND_3)_6^{3+}$ ion about the axis 1—2 of Fig. 6, one of its C_4 axes. Since this motion gives rise to an exchange between the 3 and 4, and 5 and 6, positions of Fig. 6, the lines 1b′ and 1b″ are averaged. The reorientation about the C_2 axis perpendicular to the 1—2 direction will also have the same effect. However, in this case, all the ligands must change their positions, so the potential barrier to this motion may be much higher than that to the reorientation about the C_4 axis. Therefore, the reorientation about the C_2 axes is unlikely. Although we have assumed in the above discussion that the motion at a high temperature is an isotropic one, there remains an alternative possibility that this motion is a uniaxial reorientation about any one of the four C_3 axes, because the averaged field

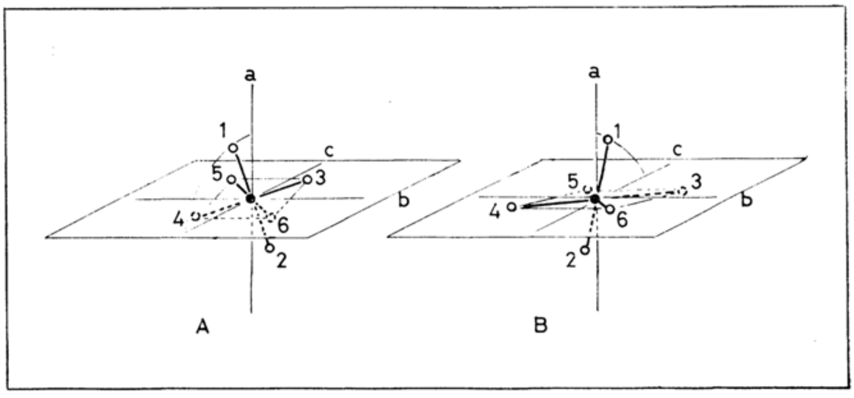

Fig. 6. Two possible orientations of $Co(ND_3)_6^{3+}$ ions at 4f sites.

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[9] P. Pyykkö and J.-L. Calais, *Kondens. Materie*, **5**, 1 (1966).

[10] D. E. O'Reilly and T. Tsang, *J. Chem. Phys.*, **46**, 1291 (1967).

gradient by such a motion is nearly zero. However, since the reorientation about the C_4 axis has already been excited at lower temperatures, it is unlikely that the motion at a high temperature is an over-all reorientation about the C_3 axis only.

At about 190°K, the lines 2 are sharp lines with a small separation, indicating an isotropic reorientation of the complex cations at the 2e sites down to this temperature. At the temperature of liquid nitrogen the over-all motions of all the complex cations must be frozen, for the absorption lines are split into many components. The spectra are so complicated that the orientation of $Co(ND_3)_6^{3+}$ ions at the 2e sites could not be determined. For the same reason the possibility of a uniaxial motion of this ion at the intermediate temperatures could not be ascertained. However, because the maximum splitting is observed when H_0 is nearly parallel to the a*, b, or c axis in the rotation patterns at the temperature of liquid nitrogen, the three Co–N bond directions in a $Co(ND_3)_6^{3+}$ ion in the 2e sites are probably nearly parallel to the a*, b, and c axes.

The proton resonance on a single crystal of $Co(NH_3)_6Cl_3$ was also measured. The resonance line exhibits a structure characteristic of a rotating three-spin system.[11] When the reorientation axis is perpendicular to the plane of the spin triangle, the spectrum is a triplet line with a peak separation of $C(3\cos^2\theta-1)$, where C is a constant determined from the proton-proton distance, and θ is the angle between H_0 and the reorientation axis. When H_0 is applied parallel to the a* axis, the spectrum at 200°K consists of two pairs of peaks with a strong center line. When H_0 is applied parallel to the b axis, only a single line with unresolved shoulders appears.

These spectra can be interpreted as follows. In the case of the H_0//a* axis, one of the reorientation axes of NH_3 is parallel to $H_0(\theta=0)$ and the other two are perpendicular to it $(\theta=\pi/2)$, so that the spectral lines consist of a triplet line with a peak separation of $2C$ and that with a peak separation of $-C$. Thus, the spectrum will be a central line with two pairs of peaks. The observed peak separation, $2C$, is about 20 gauss. Assuming the H–H distance of NH_3 to be 1.67 Å,[1] the theoretical value for the rotating three-spin system is 18.4 gauss, which is in reasonable agreement with the observed value. In the case of the H_0//b axis, one of the reorientation axes is perpendicular to H_0 and the other two make an angle of 45° with H_0, so that the spectrum consists of triplet lines with a peak separation of $-C$ and those with a peak separation of $(1/2)C$. Since the total spread of the line is small, the spectrum may be seen as a broad line with unresolved shoulders. When H_0 is applied in the direction 45° from the b axis in the bc plane, the line with two pairs of peaks was observed at 200°K, while the line with unresolved shoulders was observed at 240°K. In this case, one of the reorientation axes of NH_3 (3–4 in Fig. 6) is parallel to H_0, and the other two (5–6 and 1–2) are perpendicular to it. Since the uniaxial motion about the axis 1–2 gives rise to exchange between the 3 and 4, and 5 and 6, positions, the spectrum at 240°K consists of triplet lines, one with a separation of $-C$ (a line that originates from 1 and 2), one with a separation of $(1/2)C$ which is produced by averaging the triplet lines, one with separation of $2C$ (a line originating from 3 and 4), and one with a separation of $-C$ (a line originating from 5 and 6). Although the effect of uniaxial motion on the second moment of a powdered sample is not clear,[1] single crystal spectra show the occurrence of this motion in $Co(NH_3)_6Cl_3$. At 77°K, the proton line is a single broad line exhibiting no structure. If there are several orientations for $Co(NH_3)_6^{3+}$ ions, as suggested by the deuteron resonance, this can be understood as a single broad line resulting from the superposition of several triplet lines with various separations.

The rate of the motion can be estimated from the width of spectral lines. In the present case, the line widths at the limits of slow and rapid exchange rates can be derived from the general formula[4] as follows:

(I) Uniaxial motion

slow exchange limit $(\Omega \ll \delta)$:

$$\Delta\nu_{motion} = \Omega/2\pi \tag{2}$$

rapid exchange limit $(\Omega \gg \delta)$:

$$\Delta\nu_{motion} = \pi\delta^2/\Omega \tag{3}$$

(II) Isotropic motion

slow exchange limit $(\Omega \ll \delta)$

parallel to rotation axis:

$$\Delta\nu_{motion} = \Omega/\pi \tag{4}$$

perpendicular to rotation axis:

$$\Delta\nu_{motion} = \Omega/2\pi \tag{5}$$

rapid exchange limit $(\Omega \gg \delta)$:

$$\Delta\nu_{motion} = \left(\frac{16}{27}\right)\pi\delta^2/\Omega \tag{6}$$

$\Delta\nu_{motion}$ is the line width due to the motion, Ω is the rate of the motion, and 2δ is the frequency separation of the two sites. The rate of the motion can be calculated from the observed line width due to the motion. However, in solid samples it is difficult to estimate $\Delta\nu_{motion}$ because the signal-to-noise ratio for the broadened lines is generally poor and the absorption lines possess a dipolar width. For the $Co(ND_3)_6^{3+}$ ions at the 4f sites for which the stationary orientation has been well determined, the $\Delta\nu_{motion}$ is estimated from the observed line

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[11] E. R. Andrew and R. Bersohn, *J. Chem Phys.*, **18**, 159 (1950).

width by an approximate procedure,[12] from which Ω is derived using Eqs. (2)—(6). The results are shown in Fig. 7. One can immediately notice that there is a vast disagreement between the line connecting points of Ω from the rapid exchange limit and the line connecting points of Ω from the slow exchange limit. As will be described below, this discrepancy originates from the presence of two crystallographically-nonequivalent 4f sites for $Co(NH_3)_6{}^{3+}$ ions, ions which have approximately the same orientation but which are subject to a slightly different barrier hindering reorientation.

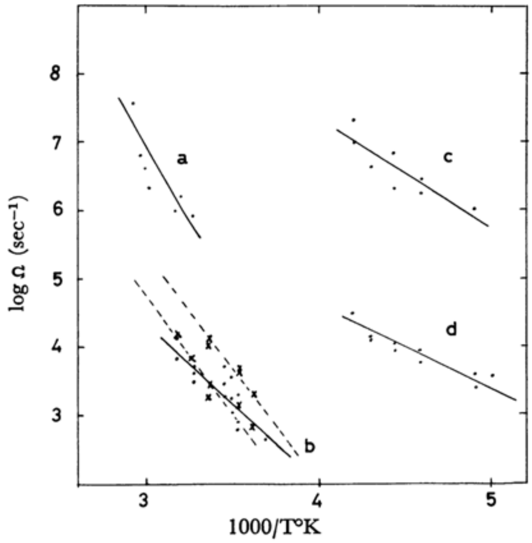

Fig. 7. Temperature dependence of reorientation rates of a $Co(ND_3)_6{}^{3+}$ ion.

a) Isotropic motion (rapid limit)
b) Isotropic motion (slow limit)
c) Uniaxial motion (rapid limit)
d) Uniaxial motion (slow limit)

As can clearly be seen in the typical example of line broadening given in Fig. 8, the lines corresponding to the stationary ions (slow-limit spectrum) and their motionally-averaged lines (rapid-limit spectrum) are simultaneously observed at some temperatures. The theory of motional averaging predicts no such spectra (the coexistence of a spectrum of a slow exchange limit and that of a fast exchange limit) in the intermediate temperature range. In tracing the motional broadening of deuteron resonance lines, there is commonly a range of temperature where the spectrum is completely washed out and unobservable between the two limiting ranges. The rather peculiar phenomenon in the present experiment can be explained by assuming that the complex cations at the two 4f sites (A and B in Fig. 6) have slightly different environments, and that, as a consequence, the cations at the two different 4f sites begin to reorient at different temperatures. The broadening process of the lines for the A and B of 4f sites cannot be observed separately except for the slow-exchange limit of the isotropic motion, because they overlap with each other in most of the crystal orientations. The presence of two 4f sites with different rates is verified by the b axis rotation spectrum, where the lines corresponding to the A and B of the 4f sites can be observed separately. The line broadening, in fact, takes place at different temperatures for the A and B sites: the lines 1a(A) and 1b(A) fade out at a lower temperature than do the lines 1a(B) and 1b(B). The rates obtained individually from these observations are also shown in Fig. 7 (by × marks). The apparent reorientation rates obtained here from the broadening of the spectrum such as that shown in Fig. 8 may, therefore, be considered to be subject to the effect of motions at the two sites, A and B. In the spectrum at 223°K of Fig. 8, the slow-limit lines (1b′ and 1b″) originate from the site with the slower exchange rate (site B),*2 while the central rapid-limit line originates from the site with the faster exchange

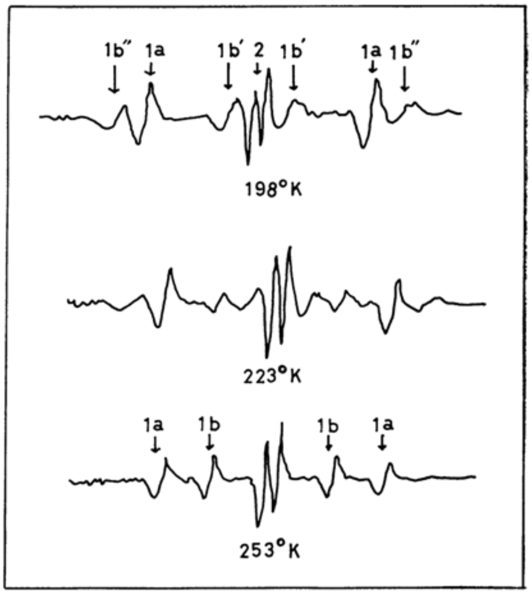

Fig. 8. Shapes of spectral lines. $H_0 // 15°$ from c axis in the bc plane.

Upper: At low temperature range (198°K), the lines 1a, 1b′ and 1b″ corresponding to the stationary ion are observed.
Lower: At high temperature range (253°K), the lines 1a and 1b corresponding to rapid reorienting ion are observed.
Middle: At intermediate temperature range (223°K), the lines 1b are observed together with the lines 1a, 1b′ and 1b″.

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[12] T. Chiba and Y. Kakiuchi, This Bulletin, **41**, 828 (1968).

rate (site A).[*2] Therefore, the rate derived from the slow limit may be predominantly of the site B, and the rate derived from the rapid limit may be predominantly of the site A. This is in qualitative agreement with the results shown in Fig. 7.

Limited as they are by various experimental conditions, the exchange rates derived in this experiment are not sufficient for the determination of potential barriers hindering the reorientations. However, we believe that the qualitative features of the motions in this crystal are rather well defined.

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[*2] The site with the larger exchange rate for the isotropic motion is A. Although the rate for the uniaxial reorientation has not been determined for each site separately, it may be reasonable to assume that for this motion the ions at the site A have also a greater exchange rate than those at the site B.