

Chlorine Nuclear Relaxation in Paramagnetic K_2IrCl_6 †

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A pure nuclear-quadrupole-resonance study of the temperature dependence of the chlorine nuclear relaxation times in the concentrated paramagnet K_2IrCl_6 is reported. It is shown that three different relaxation mechanisms contribute to the observed spin-lattice relaxation times. For temperatures less than 40°K, T_1 is dominated by the hyperfine interaction between the chlorine nuclear spins and the electron spins of the Ir^{4+} ions. At 4.2°K, the isotopic ratio of T_1 values is measured to be 1.47 ± 0.03 , in good agreement with the theoretical ratio 1.442 for a magnetic relaxation mechanism. For temperatures greater than 40°K, two quadrupole relaxation mechanisms which result from torsional oscillation and hindered rotational motions of the $[IrCl_6]^{2-}$ complexes about their symmetry axes become important, the hindered-rotation mechanism dominating the relaxation at the highest temperatures studied. The echo amplitudes were observed to decay exponentially with time; they provided temperature-independent and rather short spin-spin relaxation times. The explanation is that the resonance line is substantially narrowed by the presence of the strong electron-exchange interaction and has a width determined by the hyperfine interaction. It is shown that the low-temperature T_1 value depends only on the hyperfine parameter B , whereas the T_2 value depends only on hyperfine parameter A , a behavior which results from the large asymmetry of the transferred hyperfine interaction in $[IrCl_6]^{2-}$ ions. Using a value of the exchange parameter J taken from EPR and magnetic-susceptibility measurements, hyperfine parameters $A = 1.62 \times 10^{-3} \text{ cm}^{-1}$ and $B = 3.86 \times 10^{-5} \text{ cm}^{-1}$ are deduced from the measured relaxation rates. These values are believed to provide better than order of magnitude estimates of the true hyperfine parameters.

1. INTRODUCTION

IT has been established conclusively that covalent bonding within a paramagnetic transition-metal complex may contribute to an observable magnetic hyperfine interaction between the unpaired electron spin of the central metal ion and the nuclear spins of the surrounding ligands.^{1,2} The electron-paramagnetic-resonance (EPR) spectrum of Ir^{4+} ions substituted in an $(NH_4)_2PtCl_6$ lattice³ could be accounted for only by postulating a magnetic interaction between the unpaired electron spin of the Ir^{4+} ion and the chlorine ligand nuclear spins and by assuming a degree of covalency associated with the Ir-Cl bonds. Since this initial observation EPR experiments in other systems have provided further evidence for the existence of this type of magnetic hyperfine coupling.

The nuclear-magnetic-resonance (NMR) spectrum is also affected by the presence of a magnetic hyperfine interaction. The NMR frequency of the ligand nuclei is shifted⁴; observed paramagnetic shifts are orders of magnitude larger than chemical shifts in diamagnetic substances. In the absence of line-narrowing mechanisms the resonance would, in general, be unobservable.

However, if rapid electronic motions occur, as may result from the presence of an exchange interaction, the resonance may be exchange narrowed⁵ and a Lorentzian line profile observed.

An important contribution to the magnetic hyperfine interaction in transition-metal complexes results if the unpaired electron spin of the metal ion spends part of its time in the ligand orbitals. The magnitude of this contribution, known as the magnetic transferred hyperfine interaction, depends on the degree of covalency of the metal-ligand bonds. Information concerning the covalency may also be obtained from an interpretation of the nuclear electric quadrupole interaction using either the method suggested by Townes and Dailey⁶ or the one by Cotton and Harris.⁷ In paramagnetic transition-metal chlorides both interactions can be studied experimentally. The correlation between the two methods has been discussed by Bersohn and Shulman.⁸ They showed that, in general, the two methods measure complimentary properties.

Both EPR⁹ and nuclear-quadrupole-resonance¹⁰ (NQR) studies of the $[IrCl_6]^{2-}$ complex in K_2IrCl_6 have been carried out and the results interpreted to give a measure of the degree of covalency of the Ir-Cl bonds.

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¹ J. Owen and J. H. M. Thornley, Rept. Progr. Phys. **29**, 675 (1966).

² A. Narath, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 287.

³ J. H. E. Griffiths and J. Owen, Proc. Roy. Soc. (London) **A226**, 96 (1954).

⁴ R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963).

⁵ P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

⁶ C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

⁷ F. A. Cotton and C. B. Harris, Proc. Natl. Acad. Sci. (U.S.) **56**, 12 (1966).

⁸ R. Bersohn and R. G. Shulman, J. Chem. Phys. **45**, 2298 (1966).

⁹ J. H. M. Thornley, J. Phys. **C1**, 1024 (1968).

¹⁰ K. Ito, D. Nakamura, K. Ito, and M. Kubo, Inorg. Chem. **2**, 690 (1963).

It is the purpose of this paper to report the results of an NQR investigation of the ^{35}Cl and ^{37}Cl nuclear relaxation times in this paramagnetic transition-metal chloride. An outline of the hyperfine interaction in the $[\text{IrCl}_6]^{2-}$ ion is given in Sec. 2. The experimental data are presented in Sec. 3. Section 4 contains a discussion of the relaxation mechanisms contributing to the observed spin-lattice and spin-spin relaxation times. Magnetic hyperfine interaction parameters are calculated from the relaxation time data in Sec. 5.

2. LIGAND HYPERFINE INTERACTION IN $[\text{IrCl}_6]^{2-}$

A. Electric Nuclear Quadrupole Interaction

The structure of K_2IrCl_6 is isomorphic with that of K_2PtCl_6 .¹¹ The Bravais lattice is face-centered cubic and the basis consists of one $[\text{IrCl}_6]^{2-}$ complex at (0,0,0) and two potassium ions at $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The Ir^{4+} ion is situated at the center of a regular octahedron defined by the six chlorine ions. The lattice parameter is 9.745 Å.¹⁰

The chlorine nuclei have spin $I = \frac{3}{2}$ and site symmetry C_{4v} . Therefore the electric field gradient at the chlorine sites is nonzero and a nuclear quadrupole interaction occurs. The bonding within an $[\text{IrCl}_6]^{2-}$ complex has appreciable covalent character with the result that the electric field gradient at a chlorine site comes almost entirely from within the complex. The quadrupolar Hamiltonian for each chlorine nucleus must have axial symmetry about its Ir-Cl bond which therefore defines a convenient z axis. For the i th nucleus the Hamiltonian is of the form

$$\mathcal{H}_Q^i = \frac{1}{12} e^2 q Q [3(I_z^i)^2 - I(I+1)], \quad (1)$$

with eQ the scalar nuclear quadrupole moment and eq the axial component of the electric-field gradient.

B. Magnetic Hyperfine Interaction

A discussion of the magnetic properties of covalent XY_6 complexes was first given by Stevens.¹² Thornley⁹ has extended the discussion for the particular case of the iridium hexahalides. Initially a Hartree self-consistent-field calculation is carried out in which the electrons of the X^{4+} ion move in a potential of octahedral symmetry. The electrons from the d shell of the isolated X^{4+} ion are associated with an energy level, denoted $d\epsilon$, which has threefold orbital degeneracy. The electron configuration for $[\text{IrCl}_6]^{2-}$ is $(d\epsilon)^5$. The irreducible representation of the eigenfunctions is T_2 . Allowing for the Coulomb interactions, the eigenstates are split into terms characterized by the spin degeneracy. The ground term for $[\text{IrCl}_6]^{2-}$ is 2T_2 . The spin-orbit interaction splits the ground state into a singlet and a doublet,

with the doublet lying lowest. A calculation of the g value for the lowest level of the Ir^{4+} ion gives $g_{11} = g_{\perp} = 2$.

The EPR results of Griffiths and Owen³ on Ir^{4+} ions in $(\text{NH}_4)_2\text{PtCl}_6$ gave an isotropic g of 1.79 and indicated the presence of a magnetic hyperfine interaction between the unpaired electron spin of the metal ion and the ligand nuclear spins. Stevens showed that the results could be explained if an electron from a Cl^- ion could migrate to the Ir^{4+} ion. As far as the magnetic properties are concerned, this is equivalent to the migration of a magnetic hole from the Ir^{4+} ion to a Cl^- ion. The delocalization of the unpaired spin can be taken into account by a molecular orbital treatment in which appropriate ligand orbitals are admixed into the orbitals describing the metal ion. From the analysis of the EPR data, Griffiths and Owen concluded that the unpaired hole is 70% in the $d\epsilon$ orbitals of the Ir^{4+} ion and 5% in the p_π orbitals of each of the Cl^- ions.

The magnetic hyperfine interaction Hamiltonian must reflect the site symmetry of the chlorine nuclei and therefore for nucleus i can be written in the form

$$\mathcal{H}_M^i = \sum_j [A^{ij} I_z^i S_z^j + B^{ij} (I_x^i S_x^j + I_y^i S_y^j)], \quad (2)$$

where \mathbf{I} is the chlorine nuclear spin, \mathbf{S} the electron spin, and A^{ij} , B^{ij} are the hyperfine interaction parameters. To evaluate the contributions A_i^{ij} , B_i^{ij} due to the transferred hyperfine interaction, only the coupling between a particular chlorine nucleus and its nearest metal-ion neighbor need be considered. Stevens derived the following formulas:

$$\begin{aligned} A_i^{ij} &= -2\gamma\hbar\beta\langle 1/r^3 \rangle (16/15) N_\pi^{-2} \lambda_\pi^2, \\ B_i^{ij} &= 0, \end{aligned} \quad (3)$$

where γ is the chlorine nuclear magnetogyric ratio, β is the Bohr magneton, N_π is a normalization constant for the molecular orbitals, and λ_π is the admixture coefficient for the chlorine p_π orbitals. The radial average $\langle 1/r^3 \rangle$ is taken as that for the $3p_\pi$ orbital in a free chlorine atom. That $B_i^{ij} = 0$ is a result of the octahedral symmetry of the complex. If there is any distortion of the octahedron, then B_i^{ij} is no longer zero.

The usual dipolar interaction between the nuclear moment \mathbf{u}_{Cl}^i of a particular chlorine atom and the electronic moments \mathbf{u}_j of neighboring Ir^{4+} ions results in a second contribution to the magnetic hyperfine interaction. If the magnetic moments are taken as the point dipoles,

$$\mathbf{u}_{\text{Cl}}^i = \gamma\hbar\mathbf{I}^i, \quad \mathbf{u}_j = -g\beta\mathbf{S}^j,$$

and the separation \mathbf{R}_{ij} as the Ir-Cl bond length, then, taking account of the symmetry, it follows that the contributions A_d^{ij} , B_d^{ij} to the hyperfine interaction parameters are

$$\begin{aligned} A_d^{ij} &= \gamma g \beta \hbar (3z_{ij}^2 - R_{ij}^2) / R_{ij}^5, \\ B_d^{ij} &= -\frac{1}{2} A_d^{ij}. \end{aligned} \quad (4)$$

¹¹ W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1965), 2nd ed., Vol. 3, p. 339.

¹² K. W. H. Stevens, *Proc. Roy. Soc. (London)* **A219**, 542 (1953).

The point dipole approximation is valid for electron spins which are far removed from the chlorine nucleus of interest. However, for the electron spin within the same complex, the covalency leads to a reduction of the total dipolar interaction corresponding to the fraction of the unpaired spin that is transferred to the six ligands.^{13,14} In addition, if the electron distribution about the central metal ion does not have spherical symmetry a correction should be made for higher-order moments in the magnetic moment expansion.

Contributions to A^{ij} and B^{ij} resulting from the consideration of higher-order configurations are tabulated in the paper by Thornley.⁹

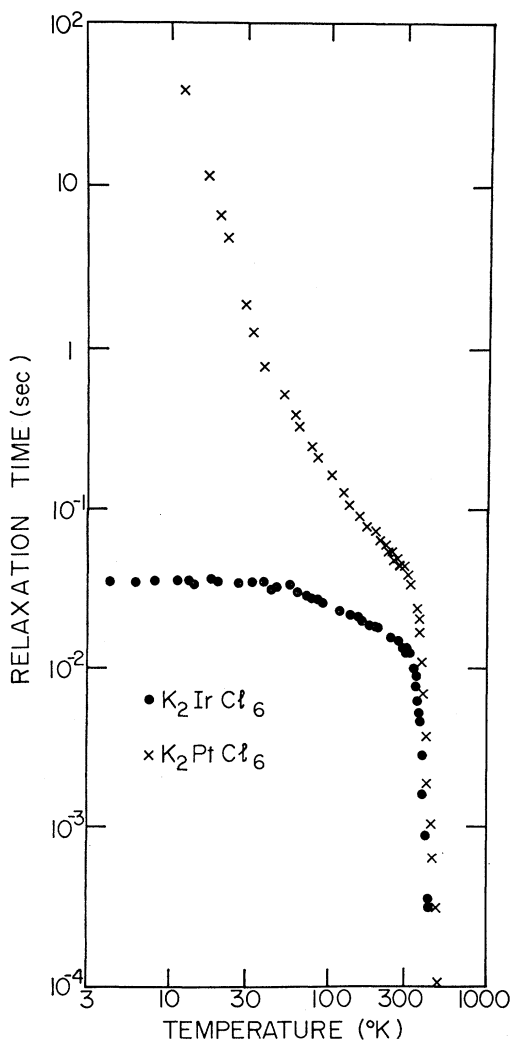


FIG. 1. Measurements of the ^{35}Cl nuclear-spin-lattice relaxation time T_1 in K_2PtCl_6 and K_2IrCl_6 as a function of temperature.

¹³ W. Marshall, in *Paramagnetic Resonance*, edited by W. Low (Academic, New York, 1963), Vol. 1.

¹⁴ W. Marshall and R. Stuart, *Phys. Rev.* **123**, 2048 (1961).

3. EXPERIMENTAL DATA

The pure nuclear-quadrupole-resonance spectra of ^{35}Cl and ^{37}Cl nuclei were observed in a sample of K_2IrCl_6 obtained from Atomergic Chemetals Co., Division of Gallard-Schlesinger Chemical Manufacturing Corp. Two pulsed magnetic resonance spectrometers of conventional design and similar to that described by Jeffrey and Armstrong¹⁵ (to be referred to hereafter as JA) were used for the experiments.

Measurements of the spin-lattice relaxation time T_1 were made for the ^{35}Cl nuclei over the temperature range from 4.2 to 450°K. The same experimental technique was employed as described in JA. The return of the nuclear magnetization was found to be exponential over the entire temperature range. The T_1 results are shown in Fig. 1 along with the data previously reported by JA for the ^{35}Cl nuclei in K_2PtCl_6 . The uncertainty in the T_1 values is about 5%.

T_1 for the ^{37}Cl nuclei was measured over the same temperature range. Particular care was taken to obtain an accurate measure of the isotopic ratio of T_1 values at 4.2 and 77°K. At each temperature and for each isotope at least 20 determinations of T_1 were obtained using a variety of spectrometer operating conditions. The results are as follows:

$$T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl}) = 1.47 \pm 0.03 \quad \text{at } 4.2^\circ\text{K},$$

$$T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl}) = 1.51 \pm 0.03 \quad \text{at } 77^\circ\text{K}.$$

The stated limits of uncertainty correspond to rms deviations.

Measurements of the spin-spin relaxation time T_2 were made for the ^{35}Cl nuclei over the same temperature range using the spin-echo technique as described in JA. The decay of the echo amplitude was found to be

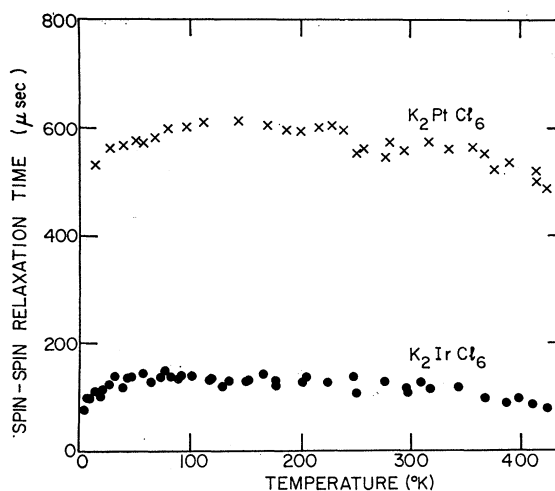


FIG. 2. Measurements of the ^{35}Cl nuclear-spin-spin relaxation time T_2 in K_2PtCl_6 and K_2IrCl_6 as a function of temperature.

¹⁵ K. R. Jeffrey and R. L. Armstrong, *Phys. Rev.* **174**, 359 (1968).

exponential for all temperatures and T_2 values could be uniquely defined. The results are shown in Fig. 2; the associated uncertainty in the T_2 values is about 10%. The T_2 data for the ^{35}Cl nuclei in K_2PtCl_6 (JA) are also shown. These values were obtained by fitting a Gaussian function to the initial portions of the echo amplitude decay curves.

For all the experiments the temperatures were measured to within 1°K using a copper-constantan thermocouple.

4. DISCUSSION OF EXPERIMENTAL DATA

A. Spin-Lattice Relaxation

The temperature dependence of the T_1 data for the ^{35}Cl resonance in K_2PtCl_6 as reported by JA is included in Fig. 1. For $T < 90^\circ\text{K}$ the behavior of T_1 was shown to be consistent with the Van Kranendonk theory.^{16,17} In this temperature range the relaxation is dominated by quadrupole-coupled Raman processes with the dominant feature of the phonon spectrum corresponding to degenerate torsional oscillations of the $[\text{PtCl}_6]^{2-}$ ions about their symmetry axes. For $90^\circ\text{K} < T < 320^\circ\text{K}$ the T_1 data decrease more slowly with temperature than can be accounted for by the Van Kranendonk theory. It is postulated that this behavior results when the amplitude of the torsional oscillations becomes so large as to invalidate the assumptions of an harmonic theory. For $T > 320^\circ\text{K}$, the T_1 data are isotope-independent, suggesting that a nonresonant process is dominating the relaxation. This behavior was interpreted as evidence for the onset of hindered rotational motion of the $[\text{PtCl}_6]^{2-}$ ions. As shown by Alexander and Tzalmona,¹⁸ the onset of hindered rotations in solids can provide a very efficient nuclear relaxation mechanism resulting in T_1 values determined solely by the residence time of the reorienting complexes at their equilibrium orientations.

Figure 1 shows that at the high temperatures the behavior of the ^{35}Cl T_1 values in K_2IrCl_6 and K_2PtCl_6 are similar, whereas at the low temperatures they are dissimilar. Below 40°K , the T_1 values in K_2IrCl_6 are temperature-independent; in K_2PtCl_6 they increase rapidly as the temperature decreases. The behavior of T_1 in K_2IrCl_6 suggests that an additional relaxation mechanism is present and that it dominates the relaxation at low temperatures. We will show that a consistent interpretation of the data can be obtained by postulating that the extra relaxation mechanism in K_2IrCl_6 is provided by the magnetic hyperfine interaction.

Relaxation caused by the presence of a magnetic hyperfine interaction has been investigated theoret-

ically by Moriya¹⁹ for the case where the Zeeman interaction is responsible for establishing the nuclear-spin eigenstates. The theory predicts that T_1 should be inversely proportional to the square of the interaction energy and to the correlation time associated with the electronic spins. In Sec. 2 it was seen that the interaction energy was proportional to the chlorine magnetogyric ratio. Therefore the isotopic ratio of the chlorine nuclear relaxation times is predicted to be equal to the square of the reciprocal isotopic ratio of the chlorine nuclear magnetogyric ratios in the region where the magnetic hyperfine interaction dominates the relaxation. That is, for this case, $T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl})$ is predicted to equal 1.442. In contrast, in a region where the electric quadrupole interaction dominates the relaxation, the isotopic ratio of the chlorine nuclear relaxation times is predicted to be equal to the square of the reciprocal of the isotopic ratio of the chlorine nuclear quadrupole moments. That is, for this case, $T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl})$ is predicted to equal 1.610.

The experimentally measured isotopic ratio of T_1 values at 4.2°K , namely 1.47 ± 0.03 is in good agreement with the theoretical prediction for a relaxation mechanism dominated by the magnetic hyperfine interaction. The experimental ratio 1.51 ± 0.03 obtained at 77°K is consistent with relaxation determined partly by the magnetic hyperfine interaction and partly by the electric quadrupole interaction.

The electron correlation time is determined by the strength of the exchange interaction between the electron spins. Since neither the exchange interaction nor the hyperfine interaction is expected to vary very much with temperature, the contribution to the nuclear relaxation rate due to the hyperfine interaction is expected to be essentially independent of the temperature. From Fig. 1 we see that $T_1(^{35}\text{Cl})$ remains almost constant at a value of 35.1 msec for $T < 40^\circ\text{K}$. For $T > 40^\circ\text{K}$, we assume that the other relaxation mechanisms mentioned become significant.

In Fig. 3, the ^{35}Cl relaxation rate in K_2IrCl_6 is plotted as a function of temperature. By subtracting the magnetic hyperfine contribution from the experimental data the points labeled "quadrupolar contribution" were obtained. The temperature dependence of the quadrupolar relaxation contribution is very similar to the experimental temperature dependence found for K_2PtCl_6 . For $50^\circ\text{K} < T < 350^\circ\text{K}$, this contribution to the relaxation is therefore assumed to result from Raman spin-phonon process with the most important contribution to the phonon spectrum resulting from torsional oscillations of the $[\text{IrCl}_6]^{2-}$ ions about their symmetry axes.

For $T > 350^\circ\text{K}$ a very rapid increase in the relaxation rate occurs. From a comparison with the K_2PtCl_6 data, this increase is attributed to the onset of hindered rotational motions of the $[\text{IrCl}_6]^{2-}$ ions. The data in this

¹⁶ J. Van Kranendonk, *Physica* **20**, 781 (1954).

¹⁷ J. Van Kranendonk and M. B. Walker, *Can. J. Phys.* **46**, 2441 (1968).

¹⁸ S. Alexander and A. Tzalmona, *Phys. Rev.* **138**, A845 (1965).

¹⁹ T. Moriya, *Progr. Theoret. Phys. (Kyoto)* **16**, 641 (1956).

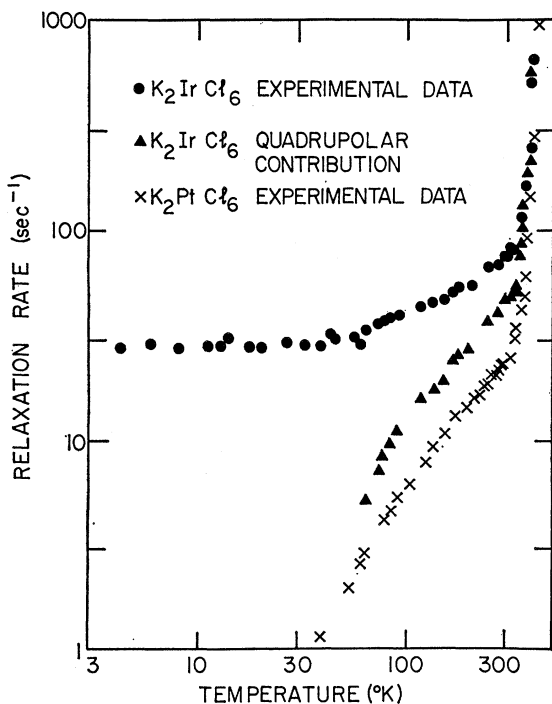


FIG. 3. Comparison of the experimental ^{35}Cl nuclear-spin-lattice relaxation rate data in K_2PtCl_6 with similar experimental data, and data corrected for the magnetic hyperfine contribution in K_2IrCl_6 .

temperature region are shown in more detail in Fig. 4. The temperature-independent relaxation rate due to the hyperfine interaction was first subtracted from the experimental data to obtain the points labeled "quadrupolar contribution." The low-temperature quadrupolar relaxation rate (Fig. 3) was extrapolated to high temperatures, as indicated by the dashed line in Fig. 4. This contribution to the relaxation was also subtracted from the experimental data to yield the points labeled "hindered rotation contribution." These points are consistent with the prediction of the temperature dependence of T_1 from the Alexander-Tzalmona theory¹⁵⁻¹⁸ that

$$T_1 = \frac{1}{6} \tau_r^0 e^{\Delta G^*/RT}, \quad (5)$$

where ΔG^* is the change in the Gibbs function required for an $[\text{IrCl}_6]^{2-}$ ion, initially in one of its equilibrium orientations, to reorient thereby arriving in a different equilibrium orientation. It follows directly from the Gibbs-Helmholtz relation and Eq. (5) that the activation enthalpy ΔH^* for a hindered rotation is given by

$$\Delta H^* = R \left(\frac{\partial \ln T_1}{\partial (1/T)} \right)_p. \quad (6)$$

From the straight-line fit to the data in Fig. 4, a value $\Delta H^* = 18.3 \pm 0.5$ kcal mole⁻¹ was deduced. This value is, to within experimental error, identical with the value

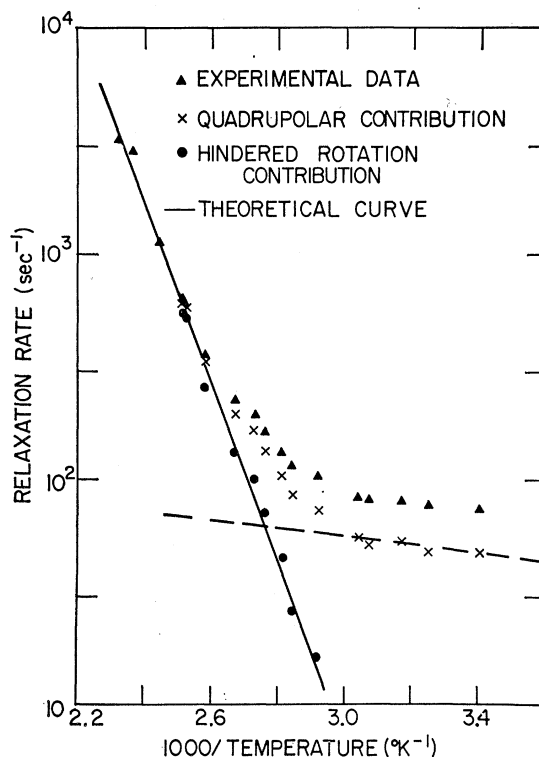


FIG. 4. ^{35}Cl nuclear-spin-lattice relaxation rate data in K_2IrCl_6 for temperatures $> 300^\circ\text{K}$. The hindered rotation contribution is extracted from the raw data. The theoretical line corresponds to an activation enthalpy $\Delta H^* = 18.3$ kcal mole⁻¹ for the onset of hindered rotations of the $[\text{IrCl}_6]^{2-}$ complexes.

$\Delta H^* = 18.8 \pm 0.5$ kcal mole⁻¹ obtained from the K_2PtCl_6 data. That is, approximately the same amount of energy is required to reorient $[\text{IrCl}_6]^{2-}$ and $[\text{PtCl}_6]^{2-}$ complexes in K_2MCl_6 lattices.

B. Spin-Spin Relaxation

The T_2 results for the ^{35}Cl nuclei in K_2IrCl_6 , presented in Fig. 2, are essentially temperature-independent over the entire range investigated. The numerical values are smaller by about a factor of 6 than the corresponding values for K_2PtCl_6 . The latter data are consistent with the value predicted from a consideration of the strength of the nuclear dipole-dipole coupling. Little change in the strength of this interaction is predicted by changing from the platinum to the iridium salt. This suggests that some other relaxation mechanism dominates the relaxation in K_2IrCl_6 . The magnetic hyperfine interaction provides such a mechanism.

In a concentrated paramagnet such as K_2IrCl_6 , the exchange interaction between electron spins is very strong (so strong, in fact, that K_2IrCl_6 is antiferromagnetic below 3.08°K). As a result, the electronic correlation time is very short and exchange narrowing of the resonance line is expected. If the resonance line

is indeed narrowed by the exchange then the Moriya theory predicts a Lorentzian line profile and consequently an exponential decay of the echo amplitude. Experimentally the echo amplitude was observed to decay exponentially at all temperatures. In contrast, the decay of the echo amplitude in K_2PtCl_6 was observed to be Gaussian. Spin-spin relaxation resulting from a magnetic hyperfine interaction is not expected to show a significant dependence on temperature, since it depends only on the squares of the hyperfine interaction parameters A^{ij} , B^{ij} and the exchange parameter J .

5. CALCULATION OF MAGNETIC HYPERFINE INTERACTION PARAMETERS FROM RELAXATION TIME DATA

The magnetic hyperfine interaction Hamiltonian was discussed in Sec. 2 where it was shown that it could be written in the form

$$\mathcal{H}_M^i = \sum_j [A^{ij} I_z^i S_z^j + B^{ij} (I_x^i S_x^j + I_y^i S_y^j)].$$

It is convenient to express the electronic spin \mathbf{S}^j of the Ir^{4+} ion as the sum of a static and a fluctuating part:

$$\mathbf{S}^j = \langle \mathbf{S}^j \rangle + \delta \mathbf{S}^j. \quad (7)$$

The thermal average $\langle \mathbf{S}^j \rangle$ is defined as

$$\langle \mathbf{S}^j \rangle = \frac{\text{Tr}(e^{-\beta \mathcal{H}_e} \mathbf{S}^j)}{\text{Tr}(e^{-\beta \mathcal{H}_e})}, \quad (8)$$

where \mathcal{H}_e is the Hamiltonian that describes the electron spin system. In a concentrated paramagnet it is an excellent approximation to take for \mathcal{H}_e only the contribution from the exchange interaction,

$$\mathcal{H}_e = \sum_{j < j'} J_{jj'} \mathbf{S}^j \cdot \mathbf{S}^{j'}. \quad (9)$$

In the paramagnetic regime with no external magnetic field applied $\langle \mathbf{S}^j \rangle = 0$. Therefore the pure NQR eigenvalues are not affected by the presence of the hyperfine interaction.

The electron-spin fluctuations $\delta \mathbf{S}^j$ are characterized by a correlation time which, because of the strong electron-exchange interaction, is short compared to the nuclear precessional frequency. As stated earlier, this leads to an exchange narrowed resonance line. The fluctuations $\delta \mathbf{S}^j$ provide a mechanism for nuclear spin relaxation. A general theory of nuclear spin relaxation in systems in which motional narrowing occurs has been proposed by Kubo and Tomita.^{20,21} Moriya¹⁹ has applied this theory to the calculation of relaxation times due to the presence of a hyperfine interaction for

the case where the nuclear Zeeman interaction gives rise to the zero-order eigenvalues.

Since $I = \frac{3}{2}$ for both chlorine isotopes, the static quadrupole interaction results in two sets of doubly degenerate levels $|\pm \frac{1}{2}\rangle$ and $|\pm \frac{3}{2}\rangle$. The return of the level populations to their equilibrium values for such a system is an exponential function of time and is described by the time constant T_1 , where²²

$$1/T_1 = 2(W_1 + W_2). \quad (10)$$

In this expression, W_1 is the transition probability for either $|\frac{3}{2}\rangle \leftrightarrow |\frac{1}{2}\rangle$ or $|\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ transitions and W_2 the transition probability for either $|\frac{3}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ or $|\frac{1}{2}\rangle \leftrightarrow |-\frac{3}{2}\rangle$ transitions. For \mathcal{H}_M the time-dependent perturbation $W_2 = 0$. In the extreme narrowing limit, it follows that

$$T_1^{-1} = \sum_{ij'} \frac{3B^{ij}B^{ij'}}{2\hbar^2} \int_0^\infty d\tau \langle \delta S_{-i}^j(\tau) \delta S_{+j'}^i \rangle, \quad (11)$$

with

$$\delta S_{-i}^j(\tau) = \exp(iI\mathcal{H}_e/\hbar) \delta S_{-i}^j \exp(-iI\mathcal{H}_e/\hbar)$$

and

$$\langle \delta S_{-i}^j(\tau) \delta S_{+j'}^i \rangle = \frac{\text{Tr}\{\exp[-\beta \mathcal{H}_e] \delta S_{-i}^j(\tau) \delta S_{+j'}^i\}}{\text{Tr}\{\exp[-\beta \mathcal{H}_e]\}}.$$

In order to simplify this expression, Moriya made the following two assumptions: (a) in the paramagnetic region, well above the Néel temperature, temperature correlations between different electron spins j and j' could be neglected; (b) the single-spin autocorrelation function $\langle \delta S_{-i}^j(\tau) \delta S_{+j'}^i \rangle$ was of the form

$$\langle \delta S_{-i}^j(\tau) \delta S_{+j'}^i \rangle = C_{-+} \exp(-\frac{1}{2}\omega_e^2 \tau^2). \quad (12)$$

Expressions for the normalization constant C_{-+} and the exchange frequency ω_e may be determined from the first two terms of a power series expansion of both sides of this equation. The final equation for T_1 is

$$T_1^{-1} = [2S(S+1)/\omega_e] (\frac{1}{2}\pi)^{1/2} (B/\hbar)^2, \quad (13)$$

where

$$\omega_e^2 = \frac{2S(S+1)}{3\hbar^2} \sum_j J_{jj}^2.$$

On the assumption that only nearest-neighbor exchange interactions are important the exchange frequency is given by

$$\omega_e^2 = 8S(S+1)J^2/\hbar^2$$

in the present case. A reasonable value for J as deduced from EPR^{23,24} and magnetic susceptibility²⁵ measure-

²² Reference 21, p. 472.

²³ J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, Proc. Roy. Soc. (London) **A250**, 84 (1958).

²⁴ E. A. Harris and J. Owen, Proc. Roy. Soc. (London) **A289**, 122 (1965).

²⁵ A. H. Cooke, R. Lazenby, F. R. McKim, J. Owen, and W. P. Wolf, Proc. Roy. Soc. (London) **A250**, 97 (1958).

²⁰ R. Kubo and T. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

²¹ A. Abragam, *Principles of Nuclear Magnetism* (Oxford U. P., London, 1961), p. 442.

ments is $(11.0 \pm 1.5)^\circ\text{K}$. Taking $T_1^{\text{exp}} = 35.1$ msec, Eq. (11) gives a value $B = 3.8(6) \times 10^{-5} \text{ cm}^{-1}$. On the basis of previous experimental tests²⁶ of the validity of the Moriya theory this determination might be expected to provide a lower limit for the hyperfine parameter B with the actual value being as much as 50% larger.

The transferred hyperfine interaction for $[\text{IrCl}_6]^{2-}$ complexes is extremely asymmetric,^{9,27} so that in first order the contribution to the B parameter is zero. In fact, the most important contribution to B results from the dipolar interaction of a chlorine nuclear spin with the electron spin of the nearest-neighbor metal ion. A theoretical estimate of B can be obtained, using a point-charge model, from the relation

$$B = -\gamma \hbar g \beta / R^3, \quad (14)$$

with R the Ir-Cl separation. As a value for R we take the Pt-Cl distance as measured in K_2PtCl_6 , namely, 2.33 Å.¹¹ A substitution of this R value, a value of $g = 1.79$ and the other appropriate constants gives $B = 2.1 \times 10^{-5} \text{ cm}^{-1}$ which is in reasonable agreement with the value obtained from the T_1 results.

To obtain an expression which relates T_2 to the hyperfine parameters constitutes a more difficult problem, since the terms in the time-dependent perturbation \mathcal{H}_M that are proportional to the B parameter couple the states $|\pm \frac{1}{2}\rangle$, thereby producing a mixed state. In order to circumvent this difficulty we will assume that the energy states can be divided into two noninteracting subsets $|\frac{1}{2}\rangle, |\frac{3}{2}\rangle$ and $|\frac{1}{2}\rangle, |-\frac{3}{2}\rangle$. This may be a reasonable assumption for $[\text{IrCl}_6]^{2-}$ complexes, since the magnitude of the B parameter is of the order of 10^{-2} times that of the A parameter. In this approximation, the value for T_2^{-1} is just the adiabatic width $T_2'^{-1}$ of the single resonance line for either subset as determined by the secular part of \mathcal{H}_M .

²⁶ M. B. Walker, Proc. Phys. Soc. (London) **87**, 45 (1966).

²⁷ E. Cipollini, J. Owen, J. H. M. Thornley, and C. Windsor, Proc. Phys. Soc. (London) **79**, 1083 (1962).

That is,¹⁹

$$T_2^{-1} = T_2'^{-1} = \sum_{jj'} \frac{A^{ij} A^{ij'}}{\hbar^2} \int_0^\infty d\tau \langle \delta S_z^j(\tau) \delta S_z^{j'} \rangle. \quad (15)$$

Under the same approximations used to deduce Eq. (13) from Eq. (11) this equation reduces to

$$T_2^{-1} = [S(S+1)/3\omega_e] (\frac{1}{2}\pi)^{1/2} (A/\hbar)^2. \quad (16)$$

That is, T_2 depends only on the hyperfine parameter A for the case $A \gg B$.

Taking $T_2^{\text{exp}} = 120 \mu\text{sec}$ and appropriate values of the other parameters, Eq. (16) yields the value $A = 16.2 \times 10^{-4} \text{ cm}^{-1}$. This result may be compared with the value $A = 8.7(1) \times 10^{-4} \text{ cm}^{-1}$ obtained from a study of isolated Ir^{4+} ions substituted in $(\text{NH}_4)_2\text{PtCl}_6$.⁹ To a first approximation, the value of the parameter A will be independent of the environment in which the $[\text{IrCl}_6]^{2-}$ complex resides. Therefore, this latter value should provide quite a reliable measure of the A parameter. The value deduced from the T_2 measurements is larger than this value by a factor of 2. This difference is therefore in large measure due to the limitations of the Moriya theory and of the additional assumption that the energy levels could be divided into two noninteracting subsets.

We have adapted the Moriya theory to the calculation of relaxation times due to the presence of an asymmetric hyperfine interaction for the case where the nuclear quadrupole interaction of a spin $\frac{3}{2}$ gives rise to the zero order eigenvalues. The theory gives an excellent qualitative description of the observed data and better than order of magnitude quantitative results.

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