# Transferred hyperfine interaction and spin-lattice relaxation time for $^{133}Cs$ in a $Cs_2CoCl_4$ single crystal

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We investigated the transferred hyperfine interaction due to transfer of the spin density from the $Co^{2+}$ ion to the $Cs^+$ ion in a $Cs_2CoCl_4$ single crystal. The transferred hyperfine interaction ($H_{hf}$) could be expressed by the linear equation $H_{hf} = [0.63T + 29.05]$ (Oe); thus, $H_{hf}$ increased with increasing temperature. Also, the $^{133}Cs$ spin-lattice relaxation time in this single crystal was measured in the temperature range of 4.2–300 K. The temperature dependence of $1/T_1$ could be described by the approximation $1/T_1 = [-9.55T + (3.22 \times 10^3)]$ $(s^{-1})$. The relaxation behavior of $^{133}Cs$ in a $Cs_2CoCl_4$ single crystal could be explained by the direct process of scattering from a single phonon. From these results, we know that the relaxation rate is proportional to the square of the transferred hyperfine field.

## I. INTRODUCTION

Tetrahedra cobalt compounds exhibit several characteristics at low temperatures which make them ideal candidates for magnetic studies. The experimental results for the heat capacity and magnetic susceptibility suggest that the compound $Cs_2CoCl_4$ undergoes a significant magnetic exchange, and there is evidence that this exchange is *XY*-like in character.[1–3] Furthermore, heat capacity results at lower temperatures confirm $Cs_2CoCl_4$ to be an example of an *XY* linear chain.[4] In this material, heat capacity measurements[4–6] indicate the existence of a long-range magnetic transition at $T_N = 0.935$ K.

The room-temperature structure of $Cs_2CoCl_4$ was determined by means of x-ray diffraction.[7] $Cs_2CoCl_4$ single crystals have an orthorhombic structure of the $\beta$-$K_2SO_4$ type and belong to the space group *Pnam* with four molecules per unit cell. The lattice parameters are $a = 9.737$ Å, $b = 7.392$ Å, and $c = 12.972$ Å at room temperature.[8] The structure consists of $Cs^+$ and tetrahedral $CoCl_4^{2-}$ ions. The Cs and Co atoms, as well as two Cl atoms [Cl(1) and Cl(2)], all lie in mirror planes. The Co-Cl distances in the $CoCl_4^{2-}$ tetrahedron are essentially identical, with four Co ions surrounded by tetrahedra of Cl atoms. This is similar to the tetrahedral cobalt salts $Cs_3CoCl_5$, $Cs_3CoBr_5$, and $Rb_3CoCl_5$.[5,9–11] In the structure of $Cs_2CoCl_4$, there are two types of inequivalent Co-ion sites. The lattice constants at $T = 0.3$ K are $a = 9.71$ Å, $b = 7.27$ Å, and $c = 12.73$ Å.[3]

The purpose of current investigations was to study the transferred hyperfine interaction due to transfer of the spin density from the $Co^{2+}$ ion to the $Cs^+$ ion in $Cs_2CoCl_4$ single crystals grown by using the slow evaporation method. Also, we measured the temperature dependence of the spin-lattice relaxation time $T_1$ for $^{133}Cs$ NMR in a $Cs_2CoCl_4$ single crystal. The measured relaxation rate was found to be proportional to the temperature in the investigated temperature range. The relation between the transferred hyperfine interaction and the relaxation rate of $^{133}Cs$ in this crystal, as discussed here, is a new result.

## II. EXPERIMENT

The single crystals of $Cs_2CoCl_4$ were grown at room temperature from an aqueous solution of a stoichiometric mixture of CsCl and $CoCl_2 \cdot 6H_2O$. The prepared samples were approximately $6 \times 6 \times 3$ $mm^3$ in size.

Nuclear magnetic resonance signals of $^{133}Cs$ in the $Cs_2CoCl_4$ single crystal were measured using a homemade pulse NMR spectrometer. The static magnetic fields were 4.70 and 1.43 T, and the frequency of the reference solution ($CsNO_3$) was set at $\omega_0/2\pi = 26.232$ and 8.002 MHz, respectively, for the $^{133}Cs$ nucleus. The $^{133}Cs$ NMR spectra were obtained by using the Hahn echo sequence ($\pi/2$-$\tau$-$\pi$), where $\pi/2 = 3.0$ $\mu$s, $\pi = 6.0$ $\mu$s, and $\tau = 100$ $\mu$s. The sample temperatures were maintained at constant values by using helium gas flow and a heater current, giving an accuracy of $\pm 0.1$ K.

## III. EXPERIMENTAL RESULTS AND ANALYSIS

### A. Transferred hyperfine interaction of $^{133}Cs$ in $Cs_2CoCl_4$

Figure 1 displays the variation of the magnetic susceptibility $\chi$ of a $Cs_2CoCl_4$ single crystal as a function of temperature. The $\chi$-$T$ measurement was carried out under a magnetic field of 4.7 T. The weight of the crystal used for the susceptibility measurement was 0.108 g. At temperatures higher than $T_N$, the magnetic susceptibility shows a typical paramagnetic behavior.

The seven-line structure of the $^{133}Cs$ NMR is a result of the quadrupole interaction of the $^{133}Cs$ ($I = 7/2$) nucleus. Only one set of seven lines was obtained for the NMR spectra of Cs even though there are four Cs nuclei per unit cell. The position of the central line for $^{133}Cs$ in $Cs_2CoCl_4$ at 4.7 T was $\nu = 26.242$ MHz. The Cs spectrum is displaced by a paramagnetic shift to the higher-frequency side relative to the reference signal obtained for the $^{133}Cs$ line from an aqueous solution of $CsNO_3$. This shift from the $^{133}Cs$ signal obtained with respect to the reference solution is related to the transferred hyperfine interaction of the $Co^{2+}$ ions in the

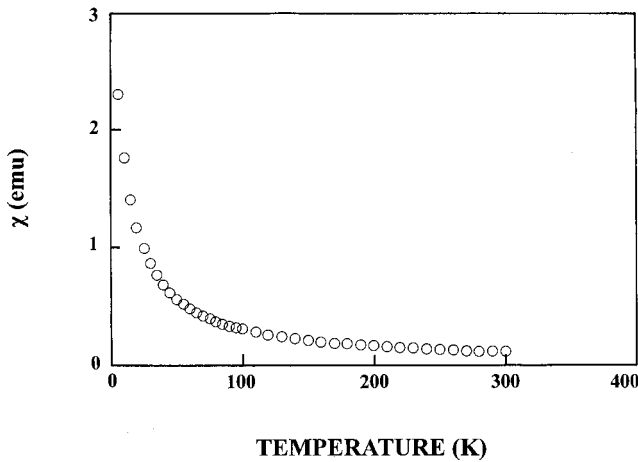FIG. 1. Temperature dependence of the magnetic susceptibility in a $Cs_2CoCl_4$ crystal.

$Cs_2CoCl_4$ crystal. The paramagnetic shift of the Cs signal in a $Cs_2CoCl_4$ single crystal as a function of temperature is shown in Fig. 2. The paramagnetic shift increases with decreasing temperature and is strongly temperature dependent. The paramagnetic shift is a direct measure of the transferred hyperfine interaction, and the most important aspect is the change in the slope of the magnetic susceptibility versus paramagnetic shift curve, which indicates the temperature dependence of the transferred hyperfine interaction. The dependence of the transferred hyperfine field on the molecular susceptibility is given by the following expression:[12–14]

$$H_{hf} = (\alpha/\chi_M) N \mu_B . \tag{1}$$

Thus the transferred hyperfine field can be obtained from the relation between the paramagnetic shift $\alpha$ and the molecular susceptibility $\chi_M$. Here $H_{hf}$ is the static hyperfine field, $N$ is Avogadro's number, and $\mu_B$ is the Bohr magneton.

The transferred hyperfine field of $^{133}Cs$ in $Cs_2CoCl_4$ was obtained over a wide temperature range as shown in Fig. 3. The measured value of the transferred hyperfine field was $H_{hf} = 202$ Oe at 287 K. The transferred hyperfine field in-
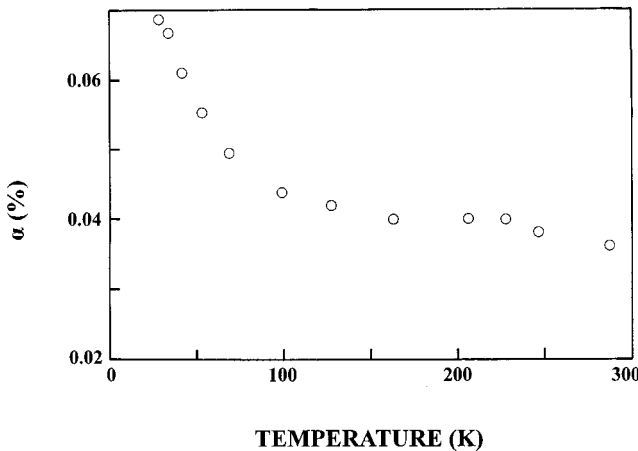


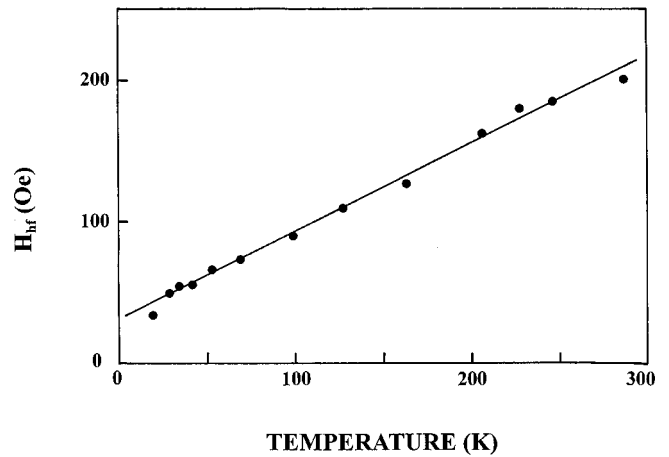FIG. 3. Transferred hyperfine field of Cs in a $Cs_2CoCl_4$ crystal as a function of temperature.

creased linearly with increasing temperature, and the $H_{hf}$ data in the paramagnetic phase could be expressed by using the linear equation

$$H_{hf} = AT + B, \tag{2}$$

where $A = 0.63$ (Oe K$^{-1}$) and $B = 29.05$ Oe.

### B. $^{133}Cs$ spin-lattice relaxation time in $Cs_2CoCl_4$

The relaxation time of $^{133}Cs$ NMR was measured at the frequency $\nu = 8.006$ MHz ($B_0 = 1.43$ T) by using a saturation recovery pulse sequence, where $T_1$ was obtained by saturating all the transition lines. Thus the traces of the magnetization in the temperature range investigated were well described by a single-exponential function. The spin-lattice relaxation rate $2W(1/T_1)$ was determined from a fit of the recovery pattern given by the following equation:[15,16]

$$S(\infty) - S(t) = S(\infty) \exp(-2Wt) = S(\infty) \exp(-t/T_1), \tag{3}$$

where $S(t)$ is the nuclear magnetization at time ($t$). The temperature dependence of $T_1^{-1}$ of Cs in a single crystal is shown in Fig. 4. The $T_1$ of $^{133}Cs$ in $Cs_2CoCl_4$ showed a short



FIG. 2. Paramagnetic shift of Cs in a $Cs_2CoCl_4$ crystal as a function of temperature.


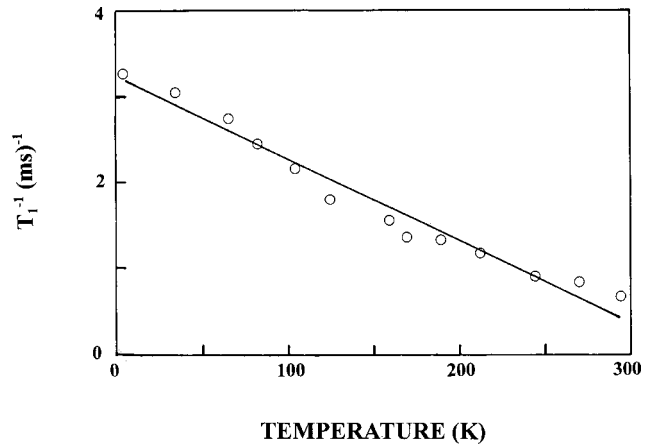
FIG. 4. Temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ for $^{133}Cs$ in a $Cs_2CoCl_4$ single crystal.

relaxation time of 1.42 ms at room temperature, and the $T_1^{-1}$ slowly decreased with increasing temperature. The rate appeared to be proportional to temperature in the temperature range 4.2–300 K, so the $T_1^{-1}$ data for Cs in this temperature range could be described by using the linear equation

$$T_1^{-1} = CT + D, \qquad (4)$$

where $C = -9.55 \ (\text{s K})^{-1}$ and $D = 3.22 \times 10^3 \ (\text{s})^{-1}$.

In many crystals, the interaction of the nuclear quadrupole moment with lattice vibrations is a vital relaxation mechanism for nuclear spin $I \geqslant 1$. The coupling can generally be written as a spin-lattice Hamiltonian[17–19]

$$H = \Sigma F^{(q)} A^{(q)}, \qquad (5)$$

where $F^{(q)}$ and $A^{(q)}$ are the lattice and spin operators, respectively, of order $q$. The lattice operators $F^{(q)}$ (hereafter, we will omit the index $q$, for brevity) can be expanded as a function of the stress tensor $\sigma$:

$$F = F_0 + F_1 \sigma + F_2 \sigma^2 + F_3 \sigma^3 + \cdots. \qquad (6)$$

At temperatures far below the melting temperature of the crystal, we can expect the thermal stress to be small, so only the first few terms in Eq. (6) are important. The term $F_1 \sigma$ represents the absorption or emission of a single phonon (direct process). The next term $F_2 \sigma^2$ indicates the emission or absorption of two phonons or absorption of one phonon followed by the emission of another (Raman process). In the direct process, the spin-lattice relaxation rate $T_1^{-1}$ is proportional to the square of the frequency $\omega_0$ and to the absolute temperature $T$ for $k_B T / \hbar \omega_0 \gg 1$. On the other hand, the Raman process allows for a relaxation rate proportional to $T^2$. The linear dependence of the relaxation rate shown in Fig. 4, which can be described by $T_1^{-1} = CT + D$, is in accordance with the single-phonon process of nuclear spin-lattice relaxation in the paramagnetic phase.

## IV. DISCUSSION AND CONCLUSION

The magnetic susceptibility for $Cs_2CoCl_4$ single crystals in the paramagnetic phase, which were grown by using the slow evaporation method, was measured with a superconducting quantum interference device (SQUID) magnetome-
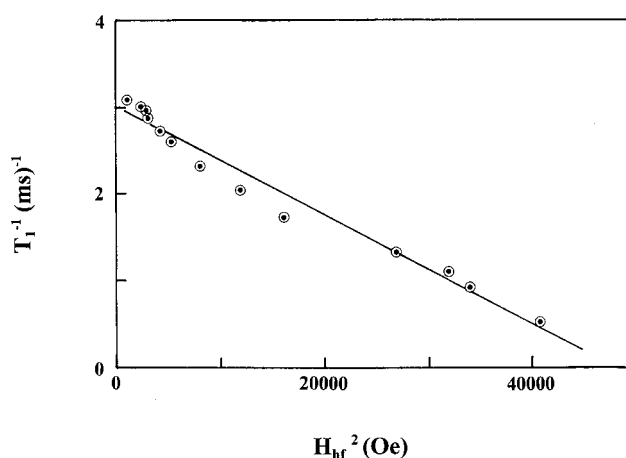


FIG. 5. Correlation between the relaxation rate $T_1^{-1}$ and the square of the transferred hyperfine field.

ter. The shift of the resonance lines in paramagnetic $Cs_2CoCl_4$ may be due to hyperfine interactions between the magnetic moment of the $Cs^+$ nucleus and the $Co^{2+}$ ions. The parameters for the transferred hyperfine field of $^{133}Cs$ in paramagnetic $Cs_2CoCl_4$ were obtained, and the transferred hyperfine field could be expressed by the linear equation $H_{hf} = [0.63T + 29.05] \ (\text{Oe})$. Also, the $H_{hf}$ due to transfer of the spin density from the $Co^{2+}$ ion to the $Cs^+$ ion increased with increasing temperature.

The relaxation process of $^{133}Cs$ for the $Cs_2CoCl_4$ single crystal was studied below room temperature. The temperature dependence of $1/T_1$ can be described by the approximation $1/T_1 = [-9.55T + (3.22 \times 10^3)] \ (\text{s}^{-1})$. From the experimental results, the relaxation behavior of $^{133}Cs$ in a $Cs_2CoCl_4$ single crystal can be explained by a direct single-phonon process in the temperature range of 4.2–300 K. The relaxation rate $T_1^{-1}$ is proportional to the square of the transferred hyperfine field, as shown in Fig. 5. The decrease in the relaxation rate is attributed to an increase in the hyperfine field. The result is consistent with the previously reported relaxation relation $T_1^{-1} \propto H_{hf}^2$.[20]

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