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Cl-35 NQR study of lattice dynamic and magnetic property of a crystalline coordination polymer {CuCA(phz)(H2O)2}n

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^{35}Cl NQR study of lattice dynamic and magnetic property of a crystalline coordination polymer $\{CuCA(phz)(H_2O)_2\}_n$

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Abstract

Copper(II) compounds $\{CuCA(phz)(H_2O)_2\}_n$ (H_2CA = chloranilic acid, phz = phenazine) having a layer structure of -$CuCA(H_2O)_2$- polymer chains and phenazine was studied by ^{35}Cl nuclear quadrupole resonance (NQR). The single NQR line observed at 35.635 MHz at 261.5 K increased to 35.918 MHz at 4.2 K. The degree of reduction of electric field gradient due to lattice vibrations was similar to that of chloranilic acid crystal. Temperature dependence of spin-lattice relaxation time, T_1, of the ^{35}Cl NQR signal below 20 K, between 20 and 210 K, and above 210 K, was explained by 1) a decrease of effective electron-spin density caused by antiferromagnetic interaction, 2) a magnetic interaction between Cl nuclear-spin and electron-spins on paramagnetic Cu(II) ions, and 3) an increasing contribution from reorientation of ligand molecules, respectively. The electron spin-exchange parameter $|J|$ between the neighboring Cu(II) electrons was estimated to be 0.33 cm^{-1} from the T_1 value of the range 20−210 K. Comparing this value with that of J = −1.84 cm^{-1} estimated from the magnetic susceptibility, it is suggested that the magnetic dipolar

coupling with the electron spins on Cu(II) ions must be the principal mechanism for the ^{35}Cl NQR spin-lattice relaxation of $\{CuCA(phz)(H_2O)_2\}_n$ but a delocalization of electron spin over the chloranilate ligand have to be taken into account.

Keywords: crystalline coordination polymer; paramagnetic; nuclear resonance; spin-lattice relaxation; spin exchange

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Introduction

Metal-complex-assembled compounds consisting of transition metals and coordinated cross-linking organic molecules can construct unique structures and realize interesting properties, such as conductivity, magnetism and optical character [1-4]. The polymer-like 1-D, 2-D and 3-D frameworks of such compounds often make various layer and porous structures like clay minerals and zeolites. These compounds with their novel structures are expected as a new field of intercalation materials. As one of them, the copper(II) compounds $\{CuCA(G)(H_2O)_2\}_n$ (H_2CA = chloranilic acid, G = H_2O, alcohols, phenazine (phz), etc.) often have a layer structure which consists of -$CuCA(H_2O)_2$- polymer chains and guest molecules, G [5-6]. The copper atom in the -$CuCA(H_2O)_2$- chain is six-coordinated by two H_2O molecules and four oxygen atoms from the two bridging chloranilate anions, CA. In $\{CuCA(phz)(H_2O)_2\}_n$, the chain of -$CuCA(H_2O)_2$- is hydrogen-bonded each other to make a layer sheet, and phenazine molecules are intercalated between -$CuCA(H_2O)_2$- polymer sheets (Fig. 1).

Nuclear Quadrupole Resonance (NQR) is an effective method to survey an electronic and dynamic state of molecules or ions in crystal. Measurements of NQR spin-lattice relaxation times, T_1, in paramagnetic substances can give us information about dynamics of unpaired electrons. For example, the correlation time, τ_f, of electron spin flip-flops has been estimated from the almost temperature independent T_1 values at low temperatures, assuming a dipolar coupling between the resonant nucleus and paramagnetic ions for $Ni(H_2O)_6SnCl_6$ [7], $Co(H_2O)_6PtCl_6$ [8], and $Cu(H_2O)_6PtCl_6$ [9]. At higher temperatures, effects of molecular motions of nearby molecules and the molecules containing the resonant nucleus itself could be observed in the temperature dependence of T_1 of the above compounds [7-9].

It is expected that both the molecular dynamics of CA and electron spin flip-flops of Cu(II) can be investigated by the ^{35}Cl NQR measurement of chloranilate anions in $\{CuCA(phz)(H_2O)_2\}_n$. In the present study, the ^{35}Cl NQR frequency, spin-lattice relaxation time, T_1, and spin-spin relaxation time, T_2, of $\{CuCA(phz)(H_2O)_2\}_n$, were measured. A molecule intercalated in -$CuCA(H_2O)_2$- sheets may have unique and different dynamics from that of the molecule in the bulk crystal because of the novel interaction between the host and the guest molecule. This is another subject to be investigated by use of ^{14}N NQR of phz in near future.

Experimental

Polycrystalline sample of $\{CuCA(phz)(H_2O)_2\}_n$ was synthesized analogously to the reported method [5]. A water solution of copper(II) chloride was pored into an ethanol-water solution of chloranilic acid and phenazine without mixing, and the deposition was grown for 3 days. The sample was identified by elemental analysis and powder X-ray diffraction.

Anal. Calcd. for $C_{18}H_{12}N_2O_6Cl_2Cu$: C, 44.42; H, 2.49; N, 5.76; Cl, 14.57,. Found: C, 44.1; H, 2.6; N, 5.6; Cl, 14.9.

The temperature dependences of the ^{35}Cl NQR frequency, spin-lattice relaxation time, T_1, and spin-spin relaxation time, T_2, of $\{CuCA(phz)(H_2O)_2\}_n$ were measured by home-build pulse NQR spectrometer based on a Matec gated amplifier model 525 from 4.2 K to 262 K. T_1 and T_2 were estimated using the inversion-recovery method and the spin-echo pulse sequence, respectively.

Results and Discussion

NQR frequency, T_1, and T_2

The sample showed only one ^{35}Cl NQR frequency at each temperature studied. The resonance frequency was 35.918 MHz at 4.2 K and decreased with increasing temperature to 35.635 MHz at 261.5 K (Fig. 2). The decrease is explainable by the following Bayer's equation [10, 11] which takes into account the effect of a single rotational lattice vibration:

$$\nu(T) = \nu(0) - \frac{3}{8\pi^2}\frac{h\nu_Q}{I_l\nu_l}\frac{1}{\exp(h\nu_l/kT)-1} \qquad (1)$$

Here

$$\nu(0) = \frac{e^2Qq}{2h}\left(1 - \frac{3}{16\pi^2}\frac{h}{I_l\nu_l}\right) \qquad (2)$$

$$\nu_Q = \frac{e^2Qq}{2h} \qquad (3)$$

and I_l and ν_l are the moment of inertia of an atomic group around a rotational axis and the frequency of the libration, respectively. The fitted line and the parameters are shown in Fig. 2 and Table 1. The slope, −1.60 kHz K^{-1}, of the fitted line in 150 − 262 K is similar to that of −1.62 kHz K^{-1} observed in the temperature dependence of ^{35}Cl NQR frequency of chloranilic acid crystal in the corresponding temperature range [12]. This means that the amplitude of molecular libration is comparable even in the coordination polymer with that in the molecular crystal. The extrapolated frequency to 0 K are 37.20 MHz and 35.918 MHz for chloranilic acid and $\{CuCA(phz)(H_2O)_2\}_n$, respectively. The decrease of the frequency of the present compound compared with that of the chloranilic acid can be explained by an increase of ionization extent.

Fig. 3 shows the temperature dependences of spin-lattice relaxation time, T_1, and spin-spin relaxation time, T_2, of the ^{35}Cl NQR signal in $\{CuCA(phz)(H_2O)_2\}_n$. Weakly temperature dependent T_1 suggests that the NQR relaxation is dominated by an magnetic coupling with the paramagnetic Cu(II) ion. However, it is noticed that T_1 shows a significant increase with decreasing temperature below 20 K, because the experimental error of T_1 and T in this temperature range is estimated to be less than ±15% and ±1%, respectively. The decreasing tendency of T_1 beyond the experimental error is also recognized above 210 K. Between 20 K and 210 K, T_1 was nearly constant at about 50 ms. The spin-spin relaxation time, T_2, estimated by assuming Gaussian decay function of the echo amplitude with the pulse separation-time gave a constant value of about 1.0 ± 0.15 ms from 4 K to 262 K.

The origin of the temperature dependence of T_1 below 20 K may be a decrease of effective electron-spin density with decreasing temperature caused by antiferromagnetic interaction, which has been indicated from the temperature dependence of magnetic susceptibility [5]. The rate of spin-lattice relaxation is proportional to χT :

$$T_1^{-1} \propto \chi T \quad . \qquad (4)$$

On the other hand, the decrease of T_1 above 210 K may be due to the contribution from small angle reorientation of ligand molecules. When the NQR relaxation is governed by molecular reorientation, T_1 is proportional to the motional correlation time τ_{re} ascribed as follows:

$$T_1 \propto \tau_{re} = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad . \qquad (5)$$

Here, τ_{re} was assumed to be expressed by the Arrhenius equation. E_a and τ_0 denote the activation energy and the correlation time in the limit of infinite temperature. The

temperature dependence of T_1 was explainable by the following equation, which accounts the contributions from small angle reorientation of ligand molecules as well as the magnetic coupling with the paramagnetic Cu(II) ions, with A = 49 $emu^{-1}\cdot mol\cdot K^{-1}\cdot s^{-1}$, B = 9.5×10^{-7} s^{-1}, E_a = 25 $kJ\cdot mol^{-1}$ and χT in the reference [5] (Fig. 3 solid line).

$$T_1^{-1} = A\chi T + \left\{ B\exp\left(\frac{E_a}{RT}\right)\right\}^{-1} \qquad (6)$$

Estimation of |J| value from T_1

The constant T_1 in the range 20−210 K is considered to be dominated by an magnetic interaction between Cl nuclear-spin and electron-spins on paramagnetic Cu(II) ions. The following expression can be obtained for T_1 originating from the dipolar coupling with paramagnetic ions having angular momentum quantum number S [8, 9]:

$$T_1^{-1} = 3\left(\frac{9}{2}\right)\gamma_N^2\gamma_e^2\eta^2\left[\frac{1}{3}S(S+1)\right]\Lambda j(\omega_Q) \quad , \qquad (7)$$

$$j(\omega_Q) = \frac{2\tau_e}{1+\omega_Q^2\tau_e^2} \quad . \qquad (8)$$

Here, γ_e and γ_N are the gyromagnetic ratio of the electron and nucleus, respectively. ω_Q is the angular NQR frequency, τ_e is the electron spin correlation time, and the geometrical factor Λ is given by

$$\Lambda = \sum_i \left\{ \left|F_i^{(1)}\right|^2 + \frac{1}{18}\left|F_i^{(0)}\right|^2 + \frac{1}{2}\left|F_i^{(2)}\right|^2 \right\} \quad . \qquad (9)$$

Here, $F_i^{(q)}$ (q = 0,1,2) are the spatial parts of the dipolar Hamiltonian between the resonant nuclear spin and the i th electron spin. They are written as

$$\left|F_i^{(0)}\right|^2 = \left(1-3\cos^2\theta_i\right)^2 / r_i^6 \quad , \qquad (10)$$

$$\left|F_i^{(1)}\right|^2 = \sin^2\theta_i \cos^2\theta_i / r_i^6 \quad , \qquad (11)$$

$$\left|F_i^{(2)}\right|^2 = \sin^4\theta_i / r_i^6 \quad . \qquad (12)$$

Here, r_i is the distance between the resonant nuclear spin and the i th electron spin, and θ_i is the angle between the z axis of EFG at the resonant nucleus and the distance vector r_i. We can approximate the function $j(\omega_Q) \approx 2\tau_e$ since the condition $\omega_Q^2 \tau_e^2 << 1$ is usually full-filled because of very short τ_e, and (7) can be written as

$$T_1^{-1} = 9\gamma_N^2 \gamma_e^2 \eta^2 S(S+1) \Lambda \tau_e \quad . \qquad (13)$$

The electron spin correlation time, τ_e, is given by the temperature-dependent electron spin-lattice relaxation time, T_{1e}, and the temperature-independent characteristic time, τ_f, for the spin flip between neighboring electrons [13] as

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_f^{-1} \quad . \qquad (14)$$

The contribution of the temperature-dependent term T_{1e}^{-1} can be assumed to be negligible in the temperature range in question since the T_1 of $\{CuCA(phz)(H_2O)_2\}_n$ is constant between 20 K and 210 K (Fig. 3), so that τ_e can be assumed to be equal to τ_f.

The spin-exchange angular frequency has been derived by Moriya [14] as

$$\omega_{ex}^2 = \frac{8}{3}\frac{J^2}{\eta^2} zS(S+1) \quad , \qquad (15)$$

considering the nearest-neighbor isotropic exchange interaction :

$$H_{ex} = -2J \boldsymbol{S}_i \cdot \boldsymbol{S}_j \quad . \qquad (16)$$

Here, z is the number of nearest neighbors of the electron-spin. The exchange parameter J can be evaluated as follows assuming the equation $\omega_{ex}^2 = \pi / (2\tau_f^2)$ [15] and putting $z = 2$ and $S = 1/2$ because of the chain structure of Cu(II) ions:

$$J = \left(\frac{\pi}{8}\right)^{1/2} \eta \tau_f^{-1} \quad . \qquad (17)$$

Thus the electron spin correlation time τ_e and then the spin-exchange parameter J between the neighboring Cu(II) electrons can be related with the T_1 value by use of eqs. (13) and (17). We obtained $\tau_e = \tau_f = 1.0\times10^{-11}$ s and $|J| = 0.48$ K (0.33 cm^{-1}) for the paramagnetic $\{CuCA(phz)(H_2O)_2\}_n$ from the observed value of $T_1 = 50$ ms and the value of $\Lambda = 1.27\times10^{44}$ cm^{-6} which is calculated by taking into account Cu(II) ions within the sphere of the radius 10 nm around the resonant nucleus in question and by assuming that the electron spins are localized on Cu(II) ions. On the other hands, $J = -1.84$ cm^{-1} was estimated from the temperature dependence of magnetic susceptibility by using the Heisenberg linear chain theory [5]. The presently derived value of $|J|$ is significantly smaller than the reported one although the magnitude can be regarded as almost the same order. It may be concluded that the principal mechanism for ^{35}Cl NQR spin-lattice relaxation of $\{CuCA(phz)(H_2O)_2\}_n$ is the magnetic dipolar coupling with the electron spins localized on Cu(II) ions. However, the localized dipole model seems not to be enough to describe the nuclear-electron interaction that is effective in the nuclear relaxation. Since the chloranilate ligand has the double O-C-C-C-O π system [16, 17], a delocalization of electron spin over the chloranilate ligand will have to be taken into account. The delocalization will result in an increase of the nuclear-electron magnetic coupling and a smaller τ_e, which corresponds to a larger $|J|$ value, will be derived from the T_1 value by use of (13).

Conclusion

Comparison of temperature coefficient of ^{35}Cl NQR frequency of

$\{CuCA(phz)(H_2O)_2\}_n$ and chloranilic acid showed that the librational amplitude of the ligand molecule in $\{CuCA(phz)(H_2O)_2\}_n$ is not so restricted, although the ligand molecule is fixed at both end to copper ions by coordination in 1-D chain of $-CuCA(H_2O)_2-$.

The value of the electron spin-exchange parameter $|J| = 0.33$ cm^{-1} estimated from the ^{35}Cl NQR T_1 is smaller than that of $|J| = 1.84$ cm^{-1} estimated from the magnetic susceptibility. This suggests that the electron spin delocalization over the ligand molecule is quite significant in the coordination polymer that contains magnetic ions.

References

[1] S. Kitagawa and M. Kondo, Bull. Chem. Soc. Jpn., 71 (1998) 1739-1753.

[2] P. J. Langley and J. Hulliger, Chem. Soc. Rev., 28 (1999) 279-291.

[3] M. Otake, Catal. Surveys Jpn., 2 (1998) 209-213.

[4] W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura and T. Sato, Microporous Mesoporous Mat., 73 (2004) 31-46.

[5] S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo and M. Katada, Inorg. Chem., 35 (1996) 4449-4461.

[6] S. Kawata, S. Kitagawa, M. Kondo and M. Katada, Synth. Metals, 71 (1995) 1917-1918.

[7] K. Horiuchi, T. Asaji and R. Ikeda, Phys. Rev. B, 50 (1994) 6169-6173.

[8] M. Mizuno, T. Asaji, A. Tachikawa and D. Nakamura, Z. Naturforsch., 46a (1991) 1103-1107.

[9] M. Mizuno, T. Asaji, D. Nakamura and K. Horiuchi, Z. Naturforsch. 45a (1990) 527-530.

[10] H. Bayer, Z. Phys., 130 (1951) 227-238.

[11] H. Chihara and N. Nakamura, Adv. Nucl. Quadrupole Reson., 4 (1980) 1-69.

[12] R. Chandramani, N. Devaraj, A. Indumathy and J. Ramakrishna, Acta. Phys. Pol., A58 (1980) 577-581.

[13] A. Birkeland and I. Svare, Phys. Scr., 18 (1978) 154-156.

[14] T. Moriya, Prog, Theor. Phys. (Kyoto), 16 (1956) 641-657.

[15] R. Kubo and K. Tomita, J. Phys. Soc. Jpn., 9 (1954) 888-919.

[16] E. K. Andersen, Acta Cryst., 22 (1967) 196-201.

[17] R. Benchekroun and J.-M. Savariault, Acta Cryst., C51 (1995) 186-188.

(Figure Caption)

Fig. 1.

The crystal structure of $\{CuCA(phz)(H_2O)_2\}_n$. Phenazine molecules are intercalated between -$CuCA(H_2O)_2$- polymer sheets being parallel to *ac* plane.

Fig. 2.

The temperature dependence of the ^{35}Cl NQR frequency in $\{CuCA(phz)(H_2O)_2\}_n$. Solid line is the least-square fit by Bayer's equation [10, 11].

Fig. 3.

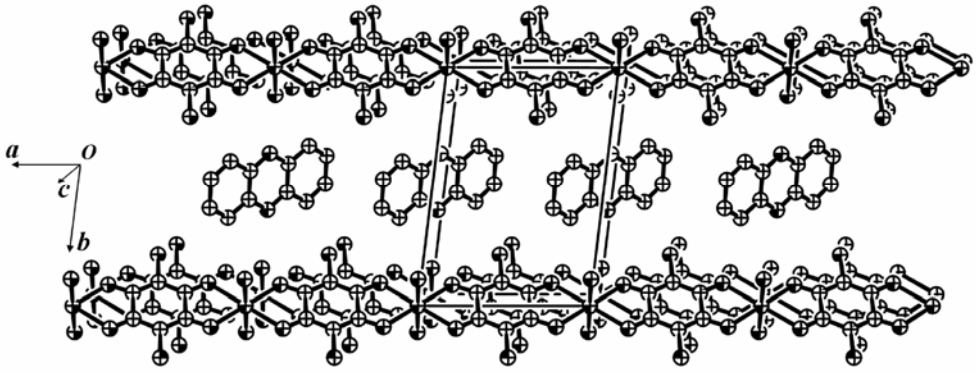
The temperature dependences of spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) of the ^{35}Cl NQR signal in $\{CuCA(phz)(H_2O)_2\}_n$ between 4 and 261.5 K. Solid line is the fit by eq. (6). Broken line and dotted line are the first and the second terms of eq. (6), respectively.

Table 1.

The fitting parameters of Bayer's equation for the temperature dependence of ^{35}Cl NQR frequency of $\{CuCA(phz)(H_2O)_2\}_n$.

$(e^2Qq/2h)$ / MHz	ν_l / cm^{-1}	I_l / kg·m^2
36.08	140	6.7×10^{-46}

Fig 1


a
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b

Fig 2

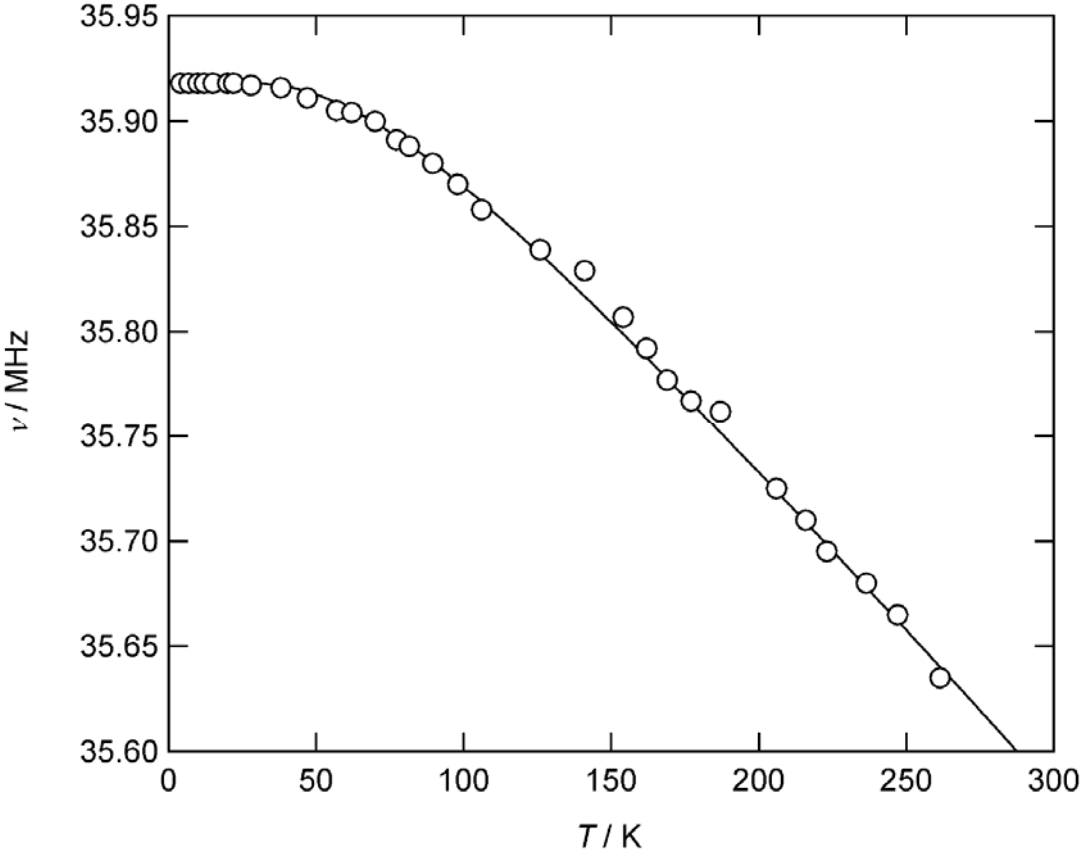
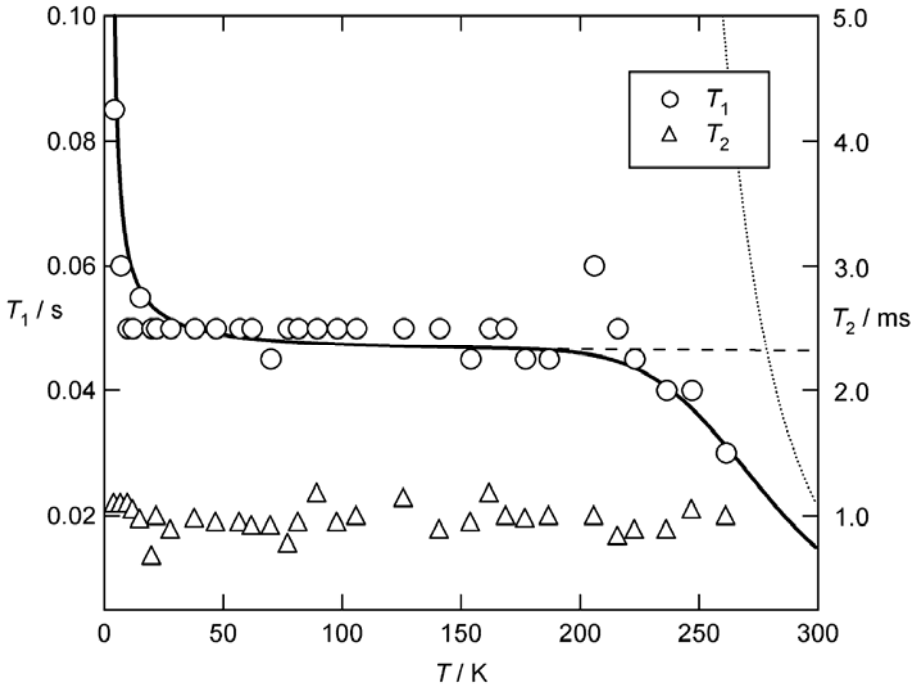

35.95
35.90
35.85
35.80
35.75
35.70
35.65
35.60
ν / MHz
0
50
100
150
200
250
300
T / K

Fig 3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0.08
0.06
0.04
0.02
T_1 / s
5.0
4.0
3.0
2.0
1.0
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T_1
T_2
0
50
100
150
200
250
300
T / K