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Effects of Vibronic Dynamics of $Cu(H_2O)_6$ Complexes and Electron Spin Relaxation in Temperature Dependence of EPR Linewidth in Diamagnetic Tutton Salt Single Crystals

S.K. Hoffmann* and J. Goslar

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

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EPR linewidth of Cu^{2+} in the Tutton salt crystals weakly depends on temperature at low temperatures and then it rapidly grows above 60 K. We present detailed results of measurements and analysis for $^{63}Cu^{2+}$ in $K_2Zn(SO_4)_2 \cdot 6H_2O$, $K_2Zn(SO_4)_2 \cdot 6D_2O$, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ and $Cs_2Zn(SO_4)_2 \cdot 6H_2O$ in a temperature range of 4.2–300 K and compare them with already published electron spin–lattice relaxation data. The relaxation contributes weakly to the linewidth which is dominated by molecular dynamics and grows exponentially with temperature. To describe this we are discussing the influence of jumps between two sites of Cu^{2+} complexes in a slow motion region where the sites are differently thermally populated. This case has not been considered so far. We have derived appropriate expressions describing the contribution of jumps to the linewidth which allows the determination of the jump rate and energy difference $\delta_{A,B}$ between the two sites being two Jahn–Teller distorted configurations of the vibronic $Cu(H_2O)_6$ complexes. The jump rate $1/\tau$ strongly depends on temperature and reaches 10^9 s^{-1} at room temperature, whereas the $\delta_{A,B}$ varies from 117 cm^{-1} for $K_2Zn(SO_4)_2 \cdot 6D_2O$ to 422 cm^{-1} for $Cs_2Zn(SO_4)_2 \cdot 6H_2O$. The comparison with vibronic level splitting, which varies in the range of 67–102 cm^{-1}, indicates that the reorientation mechanism involves phonon induced tunnelling via excited vibronic levels. These reorientations do not contribute, however, to the spin–lattice relaxation which is governed by ordinary two-phonon relaxation processes in the whole temperature range. Thus, the reorientations and spin relaxation are two independent phenomena contributing to the total linewidth.

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*corresponding author; e-mail: skh@ifmpan.poznan.pl

1. Introduction

The relationship between EPR linewidth and electron spin relaxation is well known — the faster relaxation the broader line. However, usually the relaxation is only one of a few contributions to the total linewidth [1, 2]. The relaxation contribution is due to the lifetime broadening (non-secular, non-adiabatic contribution) and can dominate in magnetically diluted solids at high temperatures (above 100 K) where it produces a strong line broadening on heating. In such a case it is possible to derive temperature dependence of the relaxation time from the linewidth temperature behaviour. This method of spin–lattice relaxation time T_1 determination has been often used for radicals and paramagnetic ions [3, 4]. The method is useful when direct methods of T_1 measurements, as electron spin echo (ESE) or saturation recovery spectroscopy, do not work. We have found such a situation for Cu^{2+} ions in the Tutton salt crystals family $M_2M^{II}(SO_4)_2 \cdot 6H_2O$ ($M = NH_4$, K, Cs; M^{II} = Zn, Cu, Cd, Mg). In series of papers we have measured T_1 time in various Tutton salts by ESE methods as reviewed in paper [5]. However, the ESE signal was detectable only below 60 K. For higher temperatures the echo dephasing rate was so fast that the ESE signal was hidden in the dead time (about 80 ns) of the pulsed spectrometer. It means that the ESR lines become homogeneously broadened when temperature increases and in fact above 60 K the lines are Lorentzian in shape and their width strongly increases on heating. It seems to suggest that the linewidth can be dominated by spin relaxation. If so, the relaxation time T_1 measurements range can be extended up to room temperature where T_1 determination from ESE experiments is not possible. This was our expectation.

Previously, we determined a linewidth temperature dependence of Cu^{2+} in $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$($NH_4Mg$) [6] and $Cs_2Zn(SO_4)_2 \cdot 6H_2O$(CsZn) [7], and in this paper we are presenting new results for $K_2Zn(SO_4)_2 \cdot 6H_2O$ (KZnH) and its deuterated analogue $K_2Zn(SO_4)_2 \cdot 6D_2O$ (KZnD). The linewidth measurements in $K_2Zn(SO_4)_2 \cdot 6H_2O : Cu^{2+}$ were used by Silver–Getz for determination of the reorientation rate of vibronic $Cu(H_2O)_6$-complexes [8], however their results were collected in the narrow low temperature range and differ slightly from our results. We have measured the linewidth in the broad temperature range (4.2–300 K) on crystals doped with ^{63}Cu to avoid isotope line broadening.

Such results were unexpected. We have found that the linewidth is determined mainly by molecular dynamics with a small contribution from relaxation only, whereas the spin–lattice relaxation is governed by the ordinary Raman processes. We have elaborated a method for calculations of the reorientation rate between two inequivalent (differently populated) potential wells dominating the linewidth at high temperatures. We have estimated also the maximum possible broadening of the EPR line due to spin–lattice relaxation for Cu^{2+} ions in single crystals.

2. Experimental

Single crystals of KZnH and KZnD were grown and Cu^{2+} doped as described previously [5, 9]. The full deuteration was achieved by fivefold recrystallization from a heavy water solution and the degree of the deuteration was controlled by ESEEM spectra as described in [5]. EPR measurements were performed on single crystals along the local z-axis (elongation axis) of the $Cu(H_2O)_6$ octahedra using a Radiopan SE/X-2547 spectrometer with 100 kHz magnetic modulation and Oxford ESR900 flow helium cryostat. The linewidth was determined in the temperature range 4.2–300 K for the hyperfine line $m_I = -1/2$ as marked by asterisk in Fig. 1. The linewidth temperature dependence of the other hyperfine lines was similar.

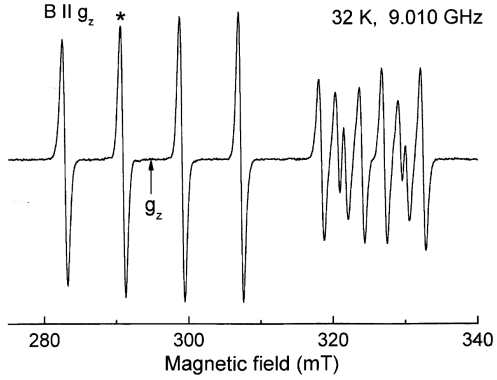

Fig. 1. EPR spectrum of Cu^{2+} in $K_2Zn(SO_4)_2 \cdot 6D_2O$ crystal recorded at 32 K along the local z-axis of the vibronic complex $Cu(H_2O)_6$. The asterisk marks the $m_I = -1/2$ hyperfine line which was excited in pulse EPR experiments and for which the linewidth temperature dependence was measured.

The concentration of Cu^{2+} ions was determined from integral intensity of the EPR lines with respect to the ultramarine blue standard as 0.9×10^{18} spins/cm^3 for KZnH and 1.2×10^{18} spins/cm^3 for KZnD. At this concentration the lines are not disturbed by a spectrum from Cu–Cu pairs which appears for higher Cu^{2+} concentrations [10].

3. Results and discussion

3.1. Linewidth temperature dependence

At low temperature range (at static limit below about 50 K) the shape of the hyperfine lines is Gaussian and electron spin echo signal can be induced. This indicates that the lines are formed from unresolved ligand hyperfine lines (spin packets). The static limit linewidth ΔB^0_{pp} of the $m_I = -1/2$ line varies from 1.3 mT for $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ to 0.24 mT for $K_2Zn(SO_4)_2 \cdot 6D_2O$. The linewidth varies with temperature as shown in Fig. 2, where the Silver–Getz results for $K_2Zn(SO_4)_2 \cdot 6H_2O$ in the narrow temperature range are added (open circles) [8].

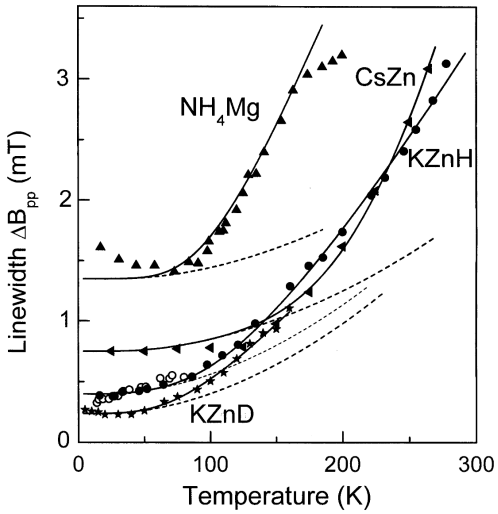

Fig. 2. Temperature variations of the peak-to-peak linewidth for Cu^{2+} in the Tutton salt crystals. Solid lines are the best fits to Eq. (8), whereas the dashed lines represent contribution from the spin–lattice relaxation processes Eq. (2).

At the low temperature range a small narrowing of the lines is observed indicating a dynamic averaging of the local magnetic field by molecular dynamics. At higher temperatures a rapid increase in $\Delta B_{\rm pp}$ appears with simultaneous continuous transition from the Gaussian to Lorentzian line shape. At these temperatures the lines become homogeneously broadened as shown by the disappearance of ESE signal. The rapid line broadening can be due to the electron relaxation processes whose effectiveness grows with temperature.

The spin–lattice relaxation rate $1/T_1$ of Cu^{2+} in the Tutton salt crystals [5] is governed by two-phonon Raman relaxation processes with temperature dependence described by the following equation:

$$\frac{1}{T_1} = bT + cT^9 \int_0^{\Theta_{\rm D}/T} \frac{x^8 \exp(x)}{[\exp(x)-1]^2} {\rm d}x, \tag{1}$$

where $\Theta_{\rm D}$ is the Debye temperature and the value of the parameters b, c, and $\Theta_{\rm D}$ are collected in Table. Using these parameters one can calculate the contribution of the T_1-processes to the static linewidth as

$$\Delta B_{\rm pp} = \frac{2}{\sqrt{3}} \frac{\hbar}{g\mu_{\rm B}} \left(\frac{1}{2T_1}\right) = \frac{2}{\sqrt{3}\gamma_{\rm e}} \frac{g_{\rm e}}{g} \left(\frac{1}{2T_1}\right) = \frac{0.13129 \times 10^{-10}}{g} \left(\frac{1}{2T_1}\right), \tag{2}$$

where $g_{\rm e} = 2.0023$, g is actual g-factor, $\Delta B_{\rm pp}$ is in [T] and T_1 in [s]. The calculated contributions are presented by the dashed lines in Fig. 2. Unexpectedly, as it is visible, this contribution is small and is overdominated by another dynamic process producing a strong increase in the linewidth with temperature but not contributing to the relaxation.

TABLE

EPR linewidth and spin–lattice relaxation data for Cu^{2+} in the Tutton salt crystals.

Cu^{2+} doped crystals	Linewidth data* $\Delta B_{pp} = \Delta B^0_{pp} + \Delta B_{pp}(1/\tau) + \Delta B_{pp}(1/2T_1)$			Spin–lattice relaxation data[b] $1/T_1 = bT + cT^9 I_8(\Theta_D/T)$	From $T_M(T)$
	ΔB^0_{pp} [mT]	$\delta_{A,B}$ [cm^{-1}]	τ_0 [10^{-9} s]	b, c, Θ_D	Δ [cm^{-1}]
KZnD	0.24	117	1.30	$b = 0$ $c = 14.5 \times 10^{-12}$ K^{-9} s^{-1} $\Theta_D = 166$ K	67[d]
KZnH	0.4 1.2[a]	167 120[a]	0.59 0.017[a]	$b = 0$ $c = 14.4 \times 10^{-12}$ K^{-9} s^{-1} $\Theta_D = 166$ K	67[d]
NH_4Mg	1.3	155	0.22	$b = 1700$ K^{-1} s^{-1} $c = 0.8 \times 10^{-12}$ K^{-9} s^{-1} $\Theta_D = 238$ K	102[c]
CsZn	0.75	422	0.034	$b = 210$ $c = 1.4 \times 10^{-12}$ K^{-9} s^{-1} $\Theta_D = 220$ K	71[b]

*This work; [a][8]; [b][9]; [c][6]; [d][18].

Errors in parameters measured in this paper ΔB^0_{pp} : ± 0.08 mT, τ_0 : $\pm 0.02 \times 10^{-9}$ s, $\delta_{A,B}$: ± 25 cm^{-1}.

The high-symmetry octahedral $Cu(H_2O)_6$ complexes in the Tutton salts undergo a strong Jahn–Teller effect resulting in three inequivalent potential wells. At low temperatures the complexes are localized in the deepest well but an increase in temperature produces reorientations (jumps) between the wells observed as progressive g-factor averaging [11]. The increase in the linewidth appears at these temperatures where an onset of the g-factors averaging can be seen. It suggests that the reorientations between potential wells producing the g-factor averaging are responsible also for the EPR line broadening.

3.2. An influence of the reorientations between two potential wells on the EPR linewidth

A relation between linewidth and reorientations of a paramagnetic centre can be generally described in terms of the relaxation matrix theory [12, 13]. In the Tutton salt crystals the situation is rather simple below room temperature since the reorientations take place between two potential wells A and B marked in Fig. 3. The energy difference between these two lowest energy wells $\delta_{A,B}$ is of the order of 100 cm^{-1} whereas the third well C has energy higher than 400 cm^{-1} and is not populated.

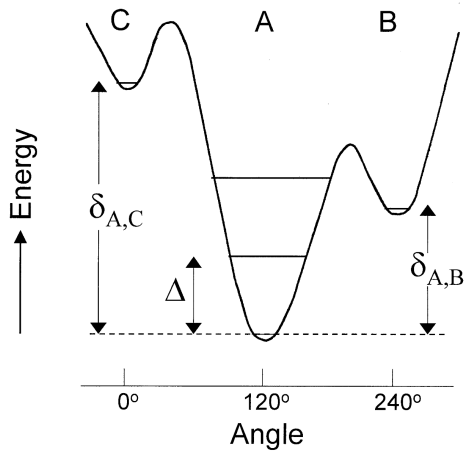

Fig. 3. Radial cross-section around the Jahn–Teller radius through the typical adiabatic potential surface of Cu^{2+} in the Tutton salt crystals. Only A and B potential wells are populated below room temperature. The energy $\delta_{A,B}$ is determined from temperature dependence of the linewidth and splitting Δ is known from ESE dephasing measurements [18].

The simple case of jumps between two sites can be considered in terms of modified Bloch equations as it has been successfully applied for exchange-type effects both in radical spectra [14] and Cu^{2+} [15, 16] but only in a case of two equally populated sites. Very often it is sufficient to know how very slow or very fast jumps affect EPR linewidth [3, 14]. In the slow motion limit, when the lifetime τ in the sites A and B is much longer than the difference between resonance frequencies at the sites, i.e. $\tau_A, \tau_B \gg (\omega_B - \omega_A)^{-1}$, the broadening of the lines appears with the peak-to-peak linewidth $\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + (\sqrt{3}\gamma_{\rm e}\tau)^{-1}$, where $\Delta B_{\rm pp}$ is the rigid lattice linewidth and τ is an average lifetime in the sites. In the fast motion limit the linewidth of the averaged line decreases with the jump rate $1/\tau$ and the effective linewidth is $\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + (2\sqrt{3})^{-1}\gamma_{\rm e}\tau(B_A - B_B)^2_{\rm rigid}$, where B_A and B_B are the line positions.

When sites A and B are inequivalent and thus have different populations n_A and n_B, the above simple model has to be extended. Such the case was considered for free radicals EPR spectra in fast motion limit only [14, 17] motivated by pronounced alternating linewidth effect in solutions. In this limit the population and motion dependent linewidth can be written as

$$\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}}\gamma_{\rm e}\tau n_A n_B (B_A - B_B)^2_{\rm rigid} \tag{3}$$

and assuming $n_B/n_A = \exp(-\delta_{A,B}/kT)$ and activated nature of reorientations with correlation time $\tau = \tau_0 \exp(\delta_{A,B}/kT)$ we can rewrite the above equation in a more convenient form

$$\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}}\gamma_{\rm e}\tau_0 \left[1 + \exp\left(-\frac{\delta_{A,B}}{kT}\right)\right]^{-2} (B_A - B_B)^2_{\rm rigid}. \tag{4}$$

Equation (4) describes a continuous narrowing of EPR line when temperature increases in the fast motion range when $\tau_A, \tau_B \ll (\omega_B - \omega_A)^{-1}$.

In this paper we are describing in detail the linewidth behaviour in the slow motion range for jumps between two inequivalent sites which has been not considered so far.

We are presenting below experimentally convenient expressions for temperature dependence of the linewidth $\Delta B_{\rm pp}$. In this motion range EPR lines show continuous broadening when temperature increases. The solution of the modified Bloch equations gives the effective linewidth of Lorentzian line

$$\Delta B^A_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}\gamma_{\rm e}\tau_A} \quad \text{and} \quad \Delta B^B_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}\gamma_{\rm e}\tau_B}. \tag{5}$$

Thus, the EPR lines of the sites A and B can have different linewidth, depending on the lifetimes τ_A and τ_B with effective reorientation rate $1/\tau = (\tau_A + \tau_B)/\tau_A\tau_B$.

Because of $n_A + n_B = 1$ and $\tau_A/\tau_B = n_A/n_B$ with $n_B/n_A = \exp(-\delta_{A,B}/kT)$ the linewidth for the most populated site A is

$$\Delta B^A_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}\gamma_{\rm e}\tau_0} \frac{\exp\left(-\delta_{A,B}/kT\right)}{\left[\exp\left(\delta_{A,B}/kT\right) + 1\right]}. \tag{6}$$

At low temperature where $kT < \delta_{A,B}$ the above equation reduces to the exponential dependence on temperature

$$\Delta B^A_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}\gamma_{\rm e}\tau_0} \exp\left(-\frac{2\delta_{A,B}}{kT}\right). \tag{7}$$

Equations (6) and (7) describe continuous broadening of the line on heating and can be used for determination of τ_0 and $\delta_{A,B}$ from experimental data $\Delta B_{\rm pp}$(T).

3.3. Dynamic and relaxation contributions to EPR linewidth

EPR lines of Cu^{2+} ions in the Tutton salt crystals exhibit strong broadening on heating above 60 K. It suggests that either spin relaxation or interwell jumps are responsible for this broadening.

Except these two contributions also a static contribution $\Delta B^0_{\rm pp}$ exists, which is experimentally determined from the temperature independent linewidth at low temperatures. At these temperatures the EPR lines are inhomogeneously broadened with the total linewidth $\Delta B^0_{\rm pp}$ determined by the Gaussian envelope of the unresolved spin packets resulting from hyperfine coupling to the distant magnetic nuclei. The $\Delta B^0_{\rm pp}$ is considerably larger for NH_4Mg because an additional coupling with protons of ammonium group is clearly lower for deuterated compound KZnD (see Table). The inhomogeneity of the lines allows us to induce ESE signals which we have used for the spin relaxation measurements [5, 6, 9]. The measurements show that the spin packets width continuously increases with temperature and above 60 K approaches the total linewidth. It means that the EPR lines become

homogeneously broadened with Lorentzian shape and their width rapidly increases with temperature.

The spin–lattice contribution to the linewidth (non-secular, non-adiabatic broadening) is due to the finite lifetime and is expressed by Eq. (2) and it is shown by dashed lines in Fig. 2. It is clearly seen that this contribution is much smaller than the interwell jumps effect. Very often, when a strong increase in an EPR linewidth with temperature is observed, it is assumed that this is due to the relaxation broadening. However, even when the T_1-time will be of the order of 1 ns at room temperature (usually is much longer) then Eq. (2) allows one to estimate the relaxation contribution as 2.5 mT. This is an upper limit of spin–lattice contribution to the EPR linewidth at room temperature. Thus, any observed increase in the linewidth from the rigid lattice limit to the room temperature larger than the above value is due to another dynamic process.

The total linewidth $\Delta B_{\rm pp}$ in the slow motion region can be written as $\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + \Delta B_{\rm pp}\ (1/\tau) + \Delta B_{\rm pp}(1/2{\rm T}_1)$ (see Table), which in an open form is as follows:

$$\Delta B_{\rm pp} = \Delta B^0_{\rm pp} + \frac{2}{\sqrt{3}\gamma_{\rm e}} \left(\frac{1}{\tau_0} \frac{\exp(-\delta_{A,B}/kT)}{[\exp(\delta_{A,B}/kT)+1]} + \frac{1}{2T_1} \right). \tag{8}$$

The $\Delta B_{\rm pp}$ plots with the fit parameters $\Delta B^0_{\rm pp}$, $\delta_{A,B}$ and τ_0 collected in Table are shown by solid lines in Fig. 2. The T_1-data in Table are taken from our paper [5]. In Table the data for KZnH from paper [8] are added. Our results for KZnH are very different from those of Silver–Getz [8]. However, they have made the linear approximation in a narrow range of linewidth temperature dependence and they considered wrongly the observed line broadening with temperature as the case of the fast motion limit.

The $\delta_{A,B}$ is the energy difference between the potential wells as shown in Fig. 3. Another energy shown in Fig. 3 is the energy Δ of the vibronic level, which we have found already from electron spin phase relaxation measurements [6, 9, 18]. The Δ values for the studied compounds are summarized in Table.

The comparison of $\delta_{A,B}$ and Δ values suggests a possible mechanism of the barrier crossing. The exponential temperature dependence of the reorientation rate, observed in our experiments, is expected for phonon-induced tunnelling involving excitations to the higher vibrational level with successive transition to a neighbour well. Looking at $\delta_{A,B}$ and Δ value in Table we conclude that the reorientation mechanism involves transitions through the first excited level in NH_4Mg, through the second excited level in KZnD and through the fourth excited level in CsZn. As a result the reorientation rate is relatively slow for the latter compound.

The spin–lattice relaxation and interwell jumps give two independent contributions to the EPR linewidth. Moreover, jumps between potential wells can also be a mechanism of the spin–lattice relaxation [19]. However, it is known that the reorientations between potential wells cannot directly produce the spin flips, i.e., cannot be a direct mechanism of the spin–lattice relaxation. Only due to

a non-orthogonality of the spin states of different potential wells, resulting from anisotropy of the g and A tensors, the reorientations can be accompanied by the spin flips with the relation rate [19, 20]:

$$\frac{1}{T_1} = \frac{2}{3}\left(\frac{\Delta g \mu_{\mathrm{B}} B + \Delta A m_{\mathrm{I}}}{h\nu}\right)^2 (\xi_x^2\xi_y^2 + \xi_y^2\xi_z^2 + \xi_z^2\xi_x^2)\frac{1}{\tau}, \tag{9}$$

where ξ_I are direction cosines of the magnetic field B with respect to the principal axes of the g and A tensors, Δg and ΔA are anisotropies of the tensors, and m_{I} is the quantum number of the adequate hyperfine line. It is easy to estimate that $1/T_1 \leq 0.02\ 1/\tau$. Thus, although the T_1 and τ have comparable value above 60 K (Fig. 4) the expected contribution from reorientations to the spin relaxation is small compared to the ordinary Raman processes in the whole temperature range. We conclude that the reorientations of the $Cu(H_2O)_6$ complexes between

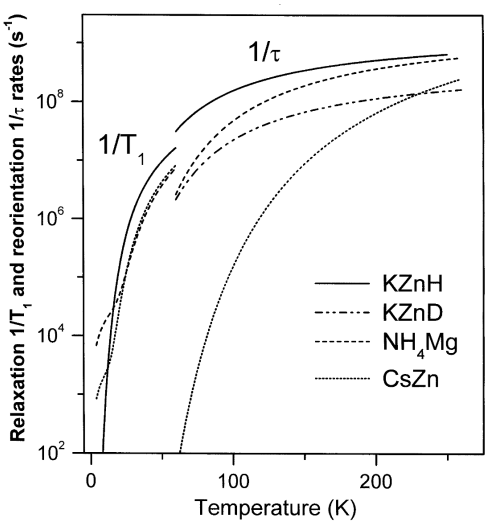

Fig. 4. Temperature dependence of the spin–lattice relaxation rate $1/T_1$ (measured by ESE methods) and reorientation rate $1/\tau$ between Jahn–Teller distorted configurations of $Cu(H_2O)_6$ (calculated from the EPR linewidth).

two potential wells and the spin–lattice relaxation are the two independent phenomena contributing to the linewidth. The former is governed by phonon-induced tunnelling via excited vibronic states and the latter is governed by ordinary two--phonon Raman relaxation processes in the whole temperature range.

4. Conclusions

The strong increase in the EPR linewidth of Cu^{2+} in the Tutton salt crystals on heating is not due to the spin–lattice relaxation which gives only a small contribution. The linewidth is determined mainly by the reorientations between

two Jahn–Teller distorted configurations, i.e. by jumps between two inequivalent potential wells. The jump rate, evaluated from new expressions valid in the slow motion region, grows exponentially with temperature and reaches $1/\tau = 10^8\ \mathrm{s}^{-1}$ at room temperature. These reorientations do not contribute, however, to the spin–lattice relaxation which is governed by ordinary two-phonon relaxation processes in the whole temperature range. Thus, the reorientations and spin relaxation are two independent phenomena contributing to the total linewidth. Assuming that the spin–lattice relaxation rate does not exceed $10^9\ \mathrm{s}^{-1}$ at room temperature, which is usual for Cu^{2+} ions, we evaluated that the maximum expected relaxation contribution to the linewidth is lower than 2.5 mT.

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