S. K. MISRA, U. ORHUN

Spin-lattice Relaxation Time of Yb"* in YbCl₃·6H₂O

The temperature dependence of the spin-lattice relaxation time $T_{Yb}$ of Yb³⁺ ions in YbCl₃·6H₂O single crystals is studied. It is found that $T_{Yb}$ has different temperature dependences in the temperature ranges $2<T<40$ K, $40<T<90$ K, $90<T<300$ K. In particular, $T_{Yb}$ is proportional to $T^{-7}$ in the temperature range 180-300 K.
X-band EPR investigations on Gd$^{3+}$-doped YbCl$_3$·6H$_2$O single crystals have been reported by Misra and Sharp [11] and by Malhotra et al. [12]. Misra and Mikolajczak [13], also reported X-band EPR results on Gd$^{3+}$-doped Yb$_x$Y$_{1-x}$Cl$_3$·6H$_2$O single crystals for x=0.25, 0.50, and 0.75. In all these cases unusual temperature dependences of the Gd$^{3+}$ EPR linewidths were found. Mitsuma [14] suggested that the fast relaxation of the paramagnetic host ions can randomly modulate the dipolar and exchange interaction between paramagnetic host and impurity ions, resulting in spin-lattice relaxation narrowing, as the temperature is raised. St-John [15] suggested that in the case of spin-lattice relaxation narrowing the impurity linewidths could be used as a probe to estimate spin-lattice relaxation times. Both Malhotra et al. [12] and Misra and Mikolajczak [13] calculated the Yb$^{3+}$ spin-lattice relaxation time in YbCl$_3$·6H$_2$O ($T_{Yb}$) using the Gd$^{3+}$ EPR linewidths as a probe.

Soeteman et al. [16] measured $T_{Yb}$ directly by the dispersion-absorption technique in YbCl$_3$·6H$_2$O single crystals; however, their measurements were confined to temperatures below 40 K only. Kalvius et al. [17] also made estimates of $T_{Yb}$ from Mossbauer technique above 40 K. No direct measurements of $T_{Yb}$ have been reported for temperatures above 40 K. $T_{Yb}$, as calculated using the Gd$^{3+}$ EPR linewidths in the temperature range 90-300 K [11, 12] do not agree with the values calculated using, either the expression of Soeteman et al. [16] or that of Kalvius et al. [17].

It is the purpose of the present paper to study the temperature dependence of $T_{Yb}$ in YbCl$_3$·6H$_2$O single crystals, with particular attention to the temperature range 90-300 K.
Malhotra et al. [23], and Misra and Nikolajczak [33] calculated $T_{\text{Yb}}$ (90-300 K) using the expression,

$$T_{\text{Yb}}^{-1} = 102(g\beta)^3 n^2 S(S+1)/3hH_{1/2}$$

(1)
given by Mitsuma [43], where $g$, $\beta$, $n$, $S$, $h$, and $H_{1/2}$ are the Landé factor, Bohr magneton, number of ions per unit volume, effective spin, Plack's constant and Gd$^{3+}$ EPR linewidth respectively. Equation (1) is based on spin-lattice relaxation narrowing phenomenon and is not valid below 180 K for Yb$^{3+}$ [3,4]. Therefore, $T_{\text{Yb}}$ calculated using (1) cannot be compared with the experimental results obtained by Soeteman et al. [6] in the temperature range 2-40 K. Mossbauer experiments by Kalvius et al. [7] above 40 K suggest a relation between temperature and $T_{\text{Yb}}$ as:

$$T_{\text{Yb}}^{-1} = 4.8 \times 10^{-11} \exp(-197/T)$$

(2)

This relation predicts $T_{\text{Yb}}$ longer by a factor of 10 at 180 K and by a factor of 50 at 300 K, as compared to those calculated using eq.(1). Furthermore, the predicted narrowing of Gd$^{3+}$ EPR linewidths as the temperature is increased cannot be explained if $T_{\text{Yb}}$ has the temperature dependence as given by eq.(2), since according to eq.(2) at higher temperatures (>90 K) the Gd$^{3+}$ EPR linewidths would narrow much less rapidly as the temperature is increased, contrary to the observations of Misra and Sharp [11] and Malhotra et al. [23].

Following Waller's theory on paramagnetic spin-lattice relaxation, assuming that $\mu H \ll kT$, where $\mu$ and $k$ are respectively the dipole moment and Boltzmann's constant, the following relation was obtained by Fierz [8],

$$T_{\text{Yb}}^{-1} = C S(S+1) T^7 \int_0^{\theta/T} \{ x^6 e^x/(e^x-1)^2 \} dx$$

(3)
where \( C \) and \( \theta \) are a constant and the Debye temperature for YbCl\(_3\)·6H\(_2\)O (=180 K) respectively. The constant \( C \) depends on the \( g \)-value, the speed of sound in the crystal, and the density of the crystal, and it is estimated by Fierz \cite{83} for certain crystals but no value has been reported for YbCl\(_3\)·6H\(_2\)O. Assuming that the spin-lattice relaxation process of Yb\(^{3+}\) ion is the main reason for the temperature dependence of Gd\(^{3+}\) EPR linewidths, the value of \( C \) can be estimated using eqs. (1) and (3).

III. CALCULATION

Using the Gd\(^{3+}\) EPR linewidths reported by Misra and Sharp \cite{13}, the Yb\(^{3+}\) spin-lattice relaxation times are calculated for different temperatures in the range 150-300 K, using eq.(1). These values are used in eq.(3) to find the value of \( C \). The average value of \( C \) is found to be \( 6.3\times10^{-4} \). So, eq.(3) can be rewritten as,

\[
T_{\text{Yb}}^{-1} = 6.3\times10^{-4} S(S+1) T^\theta \int_0^T \frac{x^6 e^x}{(e^x-1)^2} dx
\]

where \( S=3/2 \) for \( T<180 \) K, and \( S=5/2 \) for \( T>180 \) K \cite{33}. Values of \( T_{\text{Yb}} \) calculated using the data of Refs. \cite{13} and \cite{32} in connection with eq.(1), as well as values of \( T_{\text{Yb}} \) calculated using eq.(4) are given in Table 1 below.

Table 1. \( T_{\text{Yb}} \) (sec.) at different temperatures as calculated using eq.(1) (data of Refs.\cite{13}and \cite{32}) and eq.(4).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Ref.\cite{13}</th>
<th>Ref.\cite{32}</th>
<th>Eq.(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>297</td>
<td>4.0\times10^{-14}</td>
<td>7.2\times10^{-14}</td>
<td>5.7\times10^{-14}</td>
</tr>
<tr>
<td>258</td>
<td>5.1\times10^{-14}</td>
<td>7.5\times10^{-14}</td>
<td>7.7\times10^{-14}</td>
</tr>
<tr>
<td>180</td>
<td>----</td>
<td>1.0\times10^{-13}</td>
<td>3.6\times10^{-13}</td>
</tr>
<tr>
<td>173</td>
<td>4.6\times10^{-13}</td>
<td>2.9\times10^{-13}</td>
<td>3.6\times10^{-13}</td>
</tr>
<tr>
<td>153</td>
<td>5.3\times10^{-13}</td>
<td>6.85\times10^{-13}</td>
<td>4.4\times10^{-13}</td>
</tr>
<tr>
<td>90</td>
<td>5.8\times10^{-11}</td>
<td>----</td>
<td>8.5\times10^{-12}</td>
</tr>
</tbody>
</table>
Since C was found using the data given in Ref. C13, good agreement between the $T_{Yb}$ values calculated using eq.(4) and those calculated from the data of Ref. C13 is expected. These values are, however, in good agreement with the $T_{Yb}$ values calculated using the data of Ref.C23 and eq.(1) except at 90 K where the values differ as much as by 30 percent. It should, however, be noted that the use of eq.(1) to calculate $T_{Yb}$ is valid only above 180 K [3,4]. Thus $T_{Yb}$ as estimated using eq.(1) at 90 K, by Malhotra et al. C23 is not reliable.

V. CONCLUSION

The temperature dependence of $T_{Yb}$ can be divided into three temperature ranges as follows.

a) $2 < T < 40$ K: This is the only temperature range for which direct measurements of $T_{Yb}$ in YbCl$_3$·6 H$_2$O have been reported. Soetemen et al. C63 gave the temperature dependence as

$$T_{Yb}^{-1} = (1.0\pm0.1) \times 10^{-2} H^{0.47} 10^{-8} T^{0.47} J_{S},$$

where H is the external field and $J_{S}$ is a function of the Debye temperature and the temperature of the crystal.

b) $40 < T < 90$ K: There is no direct measurement of $T_{Yb}$ reported in this range. However, Mossbauer experiments by Kalvius et al. C73 suggest a temperature relation given by eq.(2). This relation does not give values consistent with the temperature dependence of Gd$^{3+}$ EPR linewidths.

c) $90 < T < 300$ K: Again, in this range, no directly measured values of $T_{Yb}$ have been reported. However, $T_{Yb}$ can be estimated from EPR linewidth data at temperatures higher than 180 K by the use of eq.(1). Furthermore, these values are in agreement with $T_{Yb}$ as calculated using eq.(4), derived from the expression of Fierz C83.
REFERENCES


STRESZCZENIE
Badano temperaturowe zależności czasu relaksacji spinowo-sieciowej $T_{\text{Yb}}$ jonów $\text{Yb}^{3+}$ w monokryształach $\text{YbCl}_3\cdot 6\text{H}_2\text{O}$. Znaleziono różne zależności $T_{\text{Yb}}$ od temperatury w przedziałach $2 < T < 40\text{K}$, $40 < T < 90\text{K}$, $90 < T < 300\text{K}$. W szczególności, $T_{\text{Yb}}$ jest proporcjonalne do $T^{-7}$ w zakresie temperatur 150-300K.

РЕЗЮМЕ
Исследовались температурные зависимости времени спин-решеточной релаксации $T_{\text{Yb}}$ ионов $\text{Yb}^{3+}$ в монокристаллах $\text{YbCl}_3\cdot \text{CH}_2\text{O}$. Обнаружены разные температурные поведения в диапазонах: $2 < T < 40\text{K}$, $40 < T < 90\text{K}$, $90 < T < 300\text{K}$. В частности — $T_{\text{Yb}}$ пропорционально $T^{-7}$ для температур 150-300 K.