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Spin-lattice Relaxation Time of Yb^{3+} in $YbCl_3 \cdot 6H_2O$

Czas relaksacji spinowo-sieciowej jonu Yb^{3+} w $YbCl_3 \cdot 6H_2O$

Время спин-решеточной релаксации иона Yb^{3+} в $YbCl_3 \cdot 6H_2O$

The temperature dependence of the spin-lattice relaxation time T_{Yb} of Yb^{3+} ions in $YbCl_3 \cdot 6\ H_2O$ 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.

I. INTRODUCTION

X-band EPR investigations on Gd^{3+}-doped $YbCl_3 6H_2O$ single crystals have been reported by Misra and Sharp [1] and by Malhotra et al. [2]. Misra and Mikolajzcak [3], also reported X-band EPR results on Gd^{3+}- doped $Yb_xY_{1-x}Cl_3 \cdot 6\ H_2O$ 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 [4] 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 [5] 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. [2] and Misra and Mikolajzcak [3] calculated the Yb^{3+} spin-lattice relaxation time in $YbCl_3 \cdot 6\ H_2O$ (T_{Yb}) using the Gd^{3+} EPR linewidths as a probe.

Soeteman et al. [6] measured T_{Yb} directly by the dispersion-absorption technique in $YbCl_3 \cdot 6H_2O$ single crystals; however, their measurements were confined to temperatures below 40 K only. Kalvius et al. [7] 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 [1,2] do not agree with the values calculated using, either the expression of Soeteman et al. [6] or that of Kalvius et al. [7].

It is the purpose of the present paper to study the temperature dependence of T_{Yb} in $YbCl_3 \cdot 6H_2O$ single crystals; with particular attention to the temperature range 90-300 K.

II. THEORY

Malhotra et al. [2], and Misra and Mikolajczak [3] calculated T_{Yb} (90-300 K) using the expression,

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

given by Mitsuma [4], where g, β, n, S, h, and $H_{1/2}$ are the Lande 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_{Yb} calculated using (1) can not 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_{Yb} as:

$$T_{Yb}^{-1} = 4.8\times10^{11}\exp(-197/T) \ . \tag{2}$$

This relation predicts T_{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 can not be explained if T_{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 [1] and Malhotra et al. [2].

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

$$T_{Yb}^{-1} = C\ S(S+1)\ T^7 \int_0^{\theta/T} \{x^6 e^x/(e^x-1)^2\}dx, \tag{3}$$

where C and θ are a constant and the Debye temperature for $YbCl_3 \cdot 6H_2O$ (≈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 [8] for certain crystals but no value has been reported for $YbCl_3 6H_2O$. 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 [1], 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 $6.3\text{x}10^{-4}$. So, eq.(3) can be rewritten as,

$$T_{Yb}^{-1} = 6.3 \cdot 10^{-4}\, S(S+1)\, T^7 \int_0^{\theta/T} \{ x^6 e^x/(e^x-1)^2 \} dx \qquad (4)$$

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

Table 1. T_{Yb}(sec.) at different temperatures as calculated using eq.(1) (data of Refs.[1]and [2]) and eq.(4).

Temperature (K)	Ref.[1]	Ref.[2]	Eq.(4)
297	$4.0\text{x}10^{-14}$	$7.2\text{x}10^{-14}$	$5.7\text{x}10^{-14}$
258	$5.1\text{x}10^{-14}$	$7.5\text{x}10^{-14}$	$7.7\text{x}10^{-14}$
180	----	$1.0\text{x}10^{-13}$	$3.6\text{x}10^{-13}$
173	$4.6\text{x}10^{-13}$	$2.9\text{x}10^{-13}$	$3.6\text{x}10^{-13}$
153	$5.3\text{x}10^{-13}$	$6.85\text{x}10^{-13}$	$4.4\text{x}10^{-13}$
90	$5.8\text{x}10^{-11}$	----	$8.5\text{x}10^{-12}$

IV. DISCUSSION

Since C was found using the data given in Ref. [1], good agreement between the T_{Yb} values calculated using eq.(4) and those calculated from the data of Ref. [1] is expected. These values are, however, in good agreement with the T_{Yb} values calculated using the data of Ref.[2] 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. [2] 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 $YbCl_3 \cdot 6H_2O$ have been reported. Soetemen et al. [6] gave the temperature dependence as

$$T_{Yb}^{-1} = (1.0 \pm 0.1)\, 10^{-2} H^4 T + 0.47\, 10^{-8} T^9 J_8 , \qquad (5)$$

where H is the external field and J_8 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. [7] 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 [8].

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STRESZCZENIE

Badano temperaturowe zależności czasu relaksacji spinowo-sieciowej T_{Yb} jonów Yb^{3+} w monokryształach $YbCl_3 \cdot 6H_2O$. Znaleziono różne zależności T_{Yb} od temperatury w przedziałach $2 < T < 40K$, $40 < T < 90K$, $90 < T < 300K$. W szczególności, T_{Yb} jest proporcjonalne do T^{-7} w zakresie temperatur 150-300K.

РЕЗЮМЕ

Исследовались температурные зависимости времени спин--решеточной релаксации T_{yb} ионов Yb^{3+} в монокристаллах $YbCl_3 \cdot CH_2O$. Обнаружены разные температурные повеления в диапазонах: $2 < T < 40$ K, $40 < T < 90$ K, $90 < T < 300$ K. В частности - T_{Yb} пропорционально T^{-7} для температур 150-300 K.