

Calculation of the paramagnetic host spin-lattice relaxation time from impurity-ion EPR linewidth

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An expression, appropriate to calculate the spin-lattice relaxation time (SLRT) of the host paramagnetic ions, using the EPR linewidths of the impurity ion, is derived by use of the second moment for crystals consisting of two different kinds of spins. Estimations have been made of the SLRT of the Yb^{3+} ion in Gd^{3+} -doped $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and LiYbF_4 single crystals, as well as that of the Co^{2+} ion in a Mn^{2+} -doped $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ single crystal. Significant differences are found in the values of SLRT as calculated using the presently derived expression from those calculated using the commonly used expression.

I. INTRODUCTION

The effect of dipolar interactions on resonance line shape was first treated by Waller,¹ and later by Broer² and Van Vleck.³ Subsequently, Anderson and Weiss⁴ presented a theory, which treats the motion of spins induced by the exchange interactions as a stochastic process, and makes it possible to describe the line shape in a fairly reasonable way. This stochastic theory was developed further by Anderson.⁵ His method goes a step further than the moment method of Van Vleck.³ More quantitative calculations of relaxation times were later reported by Mitsuma.⁶

It has been shown by Anderson and Weiss,⁴ that rapid motions of the host spins narrow the impurity EPR lines in crystals, consisting of only one paramagnetic specie. Anderson and Weiss⁴ considered the exchange interactions between the ions as the source of random spin motions, with the rate of motion being ω_e . They derived the linewidth as

$$\Delta H = \frac{10}{3} H_{\text{dip}}^2 / H_e. \quad (1)$$

In Eq. (1), H_e is not really a magnetic field but rather ω_e , expressed in magnetic-field units, and H_{dip} is the linewidth due to dipole-dipole interactions. Anderson and Weiss⁴ also showed that, subject to the condition $H_e \gg H_{\text{dip}}$, $H_{\text{dip}}^2 = h^2 \langle \Delta v^2 \rangle_{\text{av}} / g^2 \beta^2$, where h is Planck's constant, g is the Lande's factor of the paramagnetic ions, β is the Bohr magneton, and $\langle \Delta v^2 \rangle_{\text{av}}$ is the second moment (mean-square deviation from Larmor frequency). As a sample calculation, Anderson and Weiss⁴ used the second moment for a simple cubic lattice with one kind of magnetic ion, given by Van Vleck,³ as

$$\langle \Delta v^2 \rangle_{\text{av}} = 36.8 g^4 \beta^4 h^{-2} d^{-6} \left[\frac{1}{3} S(S+1) \right] \times (\lambda_1^4 + \lambda_2^4 + \lambda_3^4 - 0.187), \quad (2)$$

where d , S , and $\lambda_1, \lambda_2, \lambda_3$ are the spacing of a simple cubic lattice, the effective spin, and the direction cosines of the applied field, relative to the principal cubic axes, respec-

tively. Using Eq. (2), Anderson and Weiss⁴ showed that

$$H_{\text{dip}}^2 = 5.1 (g\beta n)^2 S(S+1), \quad (3)$$

where n is the number of host paramagnetic spins per unit volume.

In order to explain the highly temperature-dependent EPR linewidths, Mitsuma⁶ suggested that the spin-lattice relaxation process might be responsible for the narrowing of EPR lines in a way, which is similar to that caused by the exchange interactions, described above. In parallelism to the theory of Anderson and Weiss,⁴ Mitsuma⁶ derived the EPR linewidth as

$$\Delta H = \frac{10}{3} 2H_{\text{dip}}^2 / H_{\text{mod}}. \quad (4)$$

The $\frac{10}{3}$ factor, both in Eqs. (1) and (4), is due to the extreme narrowing, as pointed out by Anderson and Weiss.⁴ The factor of 2 appearing in Eq. (4) is due to Lorentzian line shape of the narrowed resonance lines. As seen from Eq. (4), the quantity H_{mod} replaces H_e in Eq. (1). Again, it is noted that H_{mod} is not a magnetic field, but rather the host-ion spin-lattice relaxation time, τ_{host} , expressed in magnetic-field units, i.e.,⁶

$$H_{\text{mod}} = h / \tau_{\text{host}} g \beta \quad (5)$$

(τ_{host} will be referred to as SLRT, hereafter).

Combining Eqs. (3), (4), and (5), τ_{host} can be expressed as

$$\tau_{\text{host}} = \frac{3h\Delta H}{102(g\beta)^3 n^2 S(S+1)}. \quad (6)$$

Thus, τ_{host} can be calculated from Eq. (6), using the experimentally observed EPR linewidth (ΔH).

As stated earlier, Eq. (3) is derived for a simple cubic lattice, consisting of only one kind of paramagnetic ion. Thus, Eq. (6) is invalid for crystals, which consist of two different kinds of paramagnetic ions.

Recently, numerous EPR experimental studies have been reported on doped crystals, wherein the paramagnetic host ions are different from impurity paramagnetic ions.

Papers continue to be published in the literature dealing with such crystals, where Eq. (6) has been employed to calculate the SLRT of the host ions (for example, see Refs. 7-12). However, as discussed above, use of Eq. (6) is not, indeed, valid in such cases.

It is the purpose of this paper to derive an equation, appropriate to calculate the SLRT of paramagnetic host ions in crystals from the impurity ion EPR linewidths, taking into account the presence of two different kinds of spins in the crystal. The derivation of this equation is

$$\langle \Delta v^2 \rangle_{\text{IIav}} = \frac{1}{3} S(S+1) h^{-2} \sum_k \left[-3g^2 \beta^2 r_{jk}^{-3} \left(\frac{3}{2} \gamma_{jk}^2 - \frac{1}{2} \right) \right]^2 + \frac{1}{3} S'(S'+1) h^{-2} \sum_{k'} \left[(-2z^2 J_{jk'}) + (1 - 3\gamma_{jk'}^2) g g' \beta^2 r_{jk'}^{-3} \right]^2. \quad (7)$$

In Eq. (7), S , r_{jk} , γ_{jk} , z , and $J_{jk'}$ represent the effective spin, the distance between the j and k ions, the direction cosine of r_{jk} with the external field, the number of electrons not in complete shells of the host ions, and the exchange integral between the host (k') and the impurity ions (j), respectively; the primed quantities describe the host ions, while the unprimed ones the impurity ion. The external field is assumed to be along the z axis.³ The impurity and host Lande factors (g, g') are assumed to be

$$\langle \Delta v^2 \rangle_{\text{IIav}} = \frac{1}{3} S'(S'+1) h^{-2} \left[N J_p^2 + (g g')^2 \beta^4 \mu_0^2 \sum_{k'} (1 - 3\gamma_{jk'}^2)^2 r_{jk'}^{-6} + 2 J_p g g' \beta^2 \mu_0 \sum_{k'} (1 - 3\gamma_{jk'}^2) r_{jk'}^{-3} \right]. \quad (8)$$

In Eq. (8), J_p is the average host-impurity pair-exchange constant. (μ_0 is the permeability constant, required for the purpose of calculations in SI units.) In reducing Eq. (7) to Eq. (8), it should be noted that J_p , the average host-impurity exchange constant,¹³ stands for the quantity $A_{jk'} = -2z^2 J_{jk'}$, as defined by Van Vleck;³ the same value (J_p) for $A_{jk'}$ has been assumed for all the neighbors taken into consideration. In magnetic field units, the full width at half peak (FWHP) of a Gaussian distribution, taking into account both the dipole-dipole and exchange interactions, can be written as

$$H_{\text{dip ex}}^2 = (2.35)^2 h^2 \langle \Delta v^2 \rangle_{\text{IIav}} / g^2 \beta^2, \quad (9)$$

where $\langle \Delta v^2 \rangle_{\text{IIav}}$ is as given by Eq. (8). Equation (9) is a generalization of Eq. (3), which is valid for crystals consisting of only one kind of paramagnetic ion, to the presence of two dissimilar kinds of paramagnetic ion in the crystal. It should be noted here, that the second moment [and, therefore, Eq. (3) which depends on it] for crystals consisting of only one kind of paramagnetic ions does not include exchange terms, whereas the second moment [and, therefore, Eq. (9) which depends on it] for crystals consisting of two different kinds of paramagnetic ions, does include exchange between dissimilar ions as well. Further, the exchange between similar ions does not appear in the expression for the second moment.³ Replacing

given in Sec. II. Sample calculations and discussion are given in Sec. III, followed by the concluding remarks in Sec. IV.

II. THEORY

The second moment, for crystals, containing two kinds of paramagnetic spins, is given by Van Vleck,³ as follows:

sufficiently different from each other, so that the resonances of these two different ions do not overlap each other.³ [It should be pointed out, here, that it is the impurity ion (unprimed) whose resonance is of interest.] Assuming that the distances between the impurity ions are sufficiently large, the first term in Eq. (7) can be neglected, compared to the other terms. If the number of the neighbors, to be considered, is limited to N , Eq. (7) reduces to

H_{dip}^2 in Eq. (4) by $H_{\text{dip ex}}^2$, one obtains

$$\Delta H = \frac{10}{3} 2 H_{\text{dip ex}}^2 / H_{\text{mod}}. \quad (10)$$

Using Eqs. (5), (8), (9), and (10) τ_{host} , the SLRT of the host ions in crystals with two different kinds of paramagnetic ingredients, can be expressed as

$$\tau_{\text{host}} = (3\Delta H g^2 \beta) / (110 h g \langle \Delta v^2 \rangle_{\text{IIav}}), \quad (11)$$

where ΔH is the impurity-ion EPR linewidth FWHP, observed experimentally; the primed Landé factor is that for the host, while the unprimed one refers to the impurity.

Equation (11), derived using the second moment for crystals with two kinds of magnetic ions, is, really, the appropriate equation for the usual EPR situation, i.e., for crystals consisting of paramagnetic host ions, doped with impurity paramagnetic ions, which are different from the host ions. One should, therefore, use Eq. (11) in order to calculate the SLRT of the host ions, rather than Eq. (6), which is valid for crystals consisting of only one kind of paramagnetic ions.

III. ILLUSTRATIVE EXAMPLES AND DISCUSSION

Using Eq. (11), the SLRT of the host paramagnetic Yb^{3+} ions in Gd^{3+} -doped $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and LiYbF_4 and that of the host paramagnetic Co^{2+} ions in Mn^{2+} -doped

TABLE I. The spin-lattice relaxation times (SLRT, in sec) of the host Yb^{3+} ions in $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and in LiYbF_4 , and that of the host Co^{2+} ions in $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ at room temperature, as calculated using the correct Eq. (11), and those calculated using the incorrect Eq. (6). The required g, g' values have also been included.

| Lattice | Impurity ion (g value) | Host ion (g' value) | SLRT [Eq. (11)] | SLRT [Eq. (6)] |
|--|------------------------------|---------------------------|-----------------------|-----------------------|
| $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ | Gd^{3+} (1.992) | Yb^{3+} (1.339) | 1.0×10^{-13} | 4.0×10^{-14} |
| LiYbF_4 | Gd^{3+} (1.992) | Yb^{3+} (1.339) | 4.3×10^{-14} | 2.5×10^{-11} |
| $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ | Mn^{2+} (1.998) | Co^{2+} (7.1) | 3.7×10^{-15} | 1.8×10^{-12} |

$\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ single crystals at room temperature are estimated in this section for illustration. Equation (11) requires rather detailed crystal structure information, such as the location of the host ions with respect to the impurity ion and the external magnetic field for the evaluation of lattice sums required in $\langle \Delta v^2 \rangle_{\text{IIav}}$ [Eq. (8)]. The following crystal structures and EPR linewidth data were used for the estimation of SLRT.

(a) Gd^{3+} -doped $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$. The structure of this crystal is monoclinic, with the unit cell parameters, $a=0.953$ nm, $b=0.643$ nm, $c=0.780$ nm, and $\beta=93^\circ 40'$.¹⁴ The average Gd^{3+} EPR linewidth, with the external magnetic field being along the z axis, at room temperature, was reported to be 14×10^{-4} T.¹⁴

(b) Gd^{3+} -doped LiYbF_4 . The structure of this crystal is tetragonal, with the space group $I4_1/a$, and the lattice constants $a=0.51335$ nm, and $c=1.0588$ nm.¹⁵ The average Gd^{3+} EPR linewidth, with the external magnetic field being along the z axis, was measured to be 10×10^{-4} T.¹⁶

(c) Mn^{2+} -doped $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$. The structure of this crystal is monoclinic,¹¹ the unit-cell parameters are not known. Therefore, the unit-cell parameters of the isostructural crystal $(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ were used: $a=0.94$ nm, $b=1.27$ nm, $c=0.63$ nm, and $\beta=106^\circ$.¹⁷ The average Mn^{2+} EPR linewidth, with the external magnetic field being along the z axis, has been reported to be 14×10^{-4} T.¹¹

In the present calculations, up to third-nearest neighbors, for the three cases, were taken into account.

SLRT of Yb^{3+} in Gd^{3+} -doped $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and Gd^{3+} -doped LiYbF_4 , as well as that of Co^{2+} in Mn^{2+} -doped $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, calculated using Eq. (11), are given in Table I, which also lists the g and g' values used. For comparison purposes, SLRT values, as calculated using the incorrect Eq. (6), are also included in Table I. The exchange constant J_p , for a Mn^{2+} - Co^{2+} pair is not known; various typical J_p values (0.2–4 GHz), were, therefore, used to calculate the SLRT of Co^{2+} . Since the resulting SLRT values did not vary in order of magnitude for these J_p values, only the average SLRT value is listed in Table I. The exchange constant for a Gd^{3+} - Yb^{3+} pair has been calculated to be 2.8 GHz in LiYbF_4 .¹⁸ As for the exchange interaction in $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$,

between Gd^{3+} and Yb^{3+} ions, it was assumed to be negligible, since the Gd^{3+} - Yb^{3+} distance in this crystal is considerably greater than that in LiYbF_4 . As seen from Table I, the SLRT calculated using the correct Eq. (11), and those calculated using the incorrect Eq. (6), are quite different from each other. It should also be noted that the Yb^{3+} SLRT, as estimated from Eq. (11), is shorter in LiYbF_4 than that in $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ at room temperature. On the other hand, the SLRT as estimated from Eq. (6) indicates that the opposite is true.^{7,16} Physically, Yb^{3+} ions are expected to have shorter SLRT in LiYbF_4 than that in $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, in accordance with that estimated from Eq. (11), since in this crystal the paramagnetic Yb^{3+} ions are packed more closely than they are in $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$. As well, one notes that the SLRT of Co^{2+} in $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, calculated from Eq. (11), is three orders of magnitude smaller than that calculated using Eq. (6).¹¹

IV. CONCLUDING REMARKS

As pointed out earlier (Sec. I), the use of Eq. (6) to calculate the host-ion SLRT in crystals with two different kinds of paramagnetic ions is not, indeed, valid, since in deriving Eq. (6), the second moment due to only one kind of paramagnetic ions is considered; the important dipolar and exchange interactions between the host and the impurity ions are not taken into account. Equation (11) is, instead, the correct expression to calculate the host ion SLRT, since it takes into account appropriately the interactions between the host and the impurity ions, in the calculation of the second moment, as well as the interactions amongst the host ions.

As seen in Sec. III, the correct Eq. (11) yields SLRT values, which are significantly different from those predicted by the incorrect Eq. (6).

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