

## On the behaviour of $\text{Er}^{3+}$ ion in tetragonal crystalline field

VINOD KUMAR, NARSINGH DASS and K CHANDRA

Department of Physics, D.B.S. College, Dehra Dun 248001

Department of Physics, University of Roorkee, Roorkee 247667

MS received 13 April 1976; in revised form 4 October 1976

**Abstract.** Crystal field parameters for  $\text{ErGaG}$  and  $\text{Er}^{3+}$  YAIG are used to compute the temperature dependence of Schottky specific heat, paramagnetic susceptibility, magnetic anisotropy,  $\mu_{\text{eff}}$  and quadrupole splitting in the range 10-400 K. The hyperfine interaction parameters  $A$  and  $B$  for  $^{168}\text{Er}$  and  $^{167}\text{Er}$  in both the systems are also obtained and in turn used to estimate the nuclear specific heat contribution. The studied parameters compare well with the available experimental results.

**Keywords.** Crystal field theory; Schottky specific heat; paramagnetic susceptibility;  $g$  and hyperfine interaction tensor.

### 1. Introduction

Crystal field theory when used semiempirically had been remarkably successful in understanding the behaviour of rare-earth ions in host crystals. In this paper crystal field investigations have been reported for garnet systems. The studies of garnets are useful in two respects; firstly they form a series of compounds with a large and asymmetric crystal field which is interesting and secondly the analysis of crystal field interactions in the paramagnetic garnets form the basis in understanding the highly anisotropic exchange interactions in rare-earth iron garnets (Wolf *et al* 1962, Wickersheim and White 1962). The case of Er is still more important because with erbium iron garnet, one can get sufficient experimental data towards better understanding of rare-earth-iron exchange interaction. Further we have studied the garnets in which iron is replaced by aluminium and gallium.

Koningstein (1967) and his co-workers (Koningstein and Schaak 1970), on the basis of their studies of absorption and fluorescence spectra of rare-earth ions substituted in garnets and also from the study of Raman spectra of TbAlG, concluded that the crystalline field at the rare-earth ion site may be considered as tetragonal. Therefore we study the Schottky specific heat in a tetragonal crystal field, the anomaly associated with it, the principal and mean paramagnetic susceptibilities, the  $g$  factors and the hyperfine interaction parameters and later compare these with the available experimental data.

### 2. Theory

The Hamiltonian for the interaction of the rare-earth ion in a crystal placed in an external magnetic field can be described as:

$$\hat{H} = \hat{H}_0 + \hat{H}_{CF} + \hat{H}_z + \hat{H}_M. \quad (1)$$

Here  $\hat{H}_0$  is free ion Hamiltonian while  $\hat{H}_{CF}$ ,  $\hat{H}_z$  and  $\hat{H}_M$  describe respectively the crystal field, the Zeeman and hyperfine interactions. For an ion with  $J$  as good quantum number in  $D_{2d}$  crystalline field:

$$\begin{aligned} \hat{H}_{CF} = & \alpha_J A_2^0 \langle r^2 \rangle \hat{O}_2^0 + \beta_J (A_4^0 \langle r^4 \rangle \hat{O}_4^0 + A_4^4 \langle r^4 \rangle \hat{O}_4^4) \\ & + \gamma_J (A_6^0 \langle r^6 \rangle \hat{O}_6^0 + A_6^4 \langle r^6 \rangle \hat{O}_6^4). \end{aligned} \quad (2)$$

In this expression  $A_n^m \langle r^n \rangle$  are derived crystal field parameters,  $\alpha_J$ ,  $\beta_J$ ,  $\gamma_J$  and  $\hat{O}_n^m$  have their usual meaning (Hutchings 1964). The diagonalisation of  $H_{CF}$  within ground  $J$  manifold gives the Stark levels which can be used to compute the gm. at. Schottky specific heat.

The eigen functions  $|a\rangle$  and  $|b\rangle$  of a Kramers doublet are so assigned that  $\langle a|J_z|b\rangle = 0$ . This in turn defines the sign of 'g' tensor (Rubin 1970), which is consistent with the Karayianis (1971) convention. Now in the presence of magnetic field, first and second order Zeeman perturbation coefficients are used to extract principal susceptibilities through Van Vleck formulation. Thus effective magnetic moment  $\mu_{eff}$  and anisotropy can also be obtained.

The  $\hat{H}_M$  Hamiltonian accounts for the hyperfine structure produced by the interaction of internal magnetic field and electric field gradient (EFG) with the nuclear magnetic dipole moment and electric quadrupole moment (Ofer *et al* 1968, Elliot and Stevens 1953) respectively. The temperature dependence of quadrupole splitting for <sup>166</sup>Er (80.6 keV) is also computed through the relation:

$$\begin{aligned} \langle \Delta E_Q \rangle_T = & (e^2 Q/8) [(1 - R) \langle r^{-3} \rangle_{4f} \alpha_J \langle 3J_z^2 - J(J+1) \rangle_T \\ & + 4(1 - \gamma_\infty) A_2^0 \langle r^2 \rangle / e^2 \langle r^2 \rangle_{4f} (1 - \sigma_2)]. \end{aligned} \quad (3)$$

Here the symbols have their usual meaning. At very low temperatures, the effect of hyperfine structure shows up in the specific heat and its contribution can be estimated with  $P$  referred to the effect of lowest Stark level only (Bleaney 1950).

### 3. Calculations

The  $D_{15/2}$  representation of the spherical rotation group, corresponding to the ground term  $^4I_{15/2}$  of Er<sup>3+</sup> ion ( $4f^{11}$ ), in presence of a tetragonal crystalline field is transformed according to the expansion:  $D_{15/2} \rightarrow 4(^2\Gamma_6 + ^2\Gamma_7)$  and yields eight Kramers doublets designated by crystal quantum numbers as  $\mu = \pm 3/2 (^2\Gamma_6)$  and  $\mu = \pm 1/2 (^2\Gamma_7)$ . The optical spectra of Er<sup>3+</sup> in garnets were studied by Koningstein and Geusic (1964). In the case of Er<sup>3+</sup> Wong (1961) found that the first excited term  $^4I_{13/2}$  is separated by 6776 cm<sup>-1</sup> from the ground  $^4I_{15/2}$  term. In view of this large separation, the physical properties at room or lower temperatures will be determined by the ground manifold and as such calculations are performed within that state only. The Stark levels and corresponding eigen vectors in ground  $J$  manifold are obtained by employing the operator equivalent parameters derived by Kuse (1974), from the intermediate coupling scheme in Er<sup>3+</sup> ion wave functions of Rajnak (1965). The crystal field parameters (Orlich

Table 1. Crystal field parameters (in  $\text{cm}^{-1}$ ) for Garnets in  $D_{2d}$  site symmetry.

System	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r_4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_4^4 \langle r^4 \rangle$	$A_6^4 \langle r^4 \rangle$	Ref.
ErGaG	0.0	-260.0	40.0	920.0	595.0	Orlich <i>et al.</i> (1970)
Er <sup>3+</sup> : YAlG	260.0	-160.0	45.0	800.0	-710.0	„

*et al* 1970) used in the calculations are listed in table 1. Thus the temperature dependences of Schottky specific heat and the magnetic susceptibilities are computed in the range 10–400 K. The calculations of hyperfine structure parameters are carried out for Mossbauer nuclei <sup>100</sup>Er and non zero ground state nuclear spin case of <sup>16</sup>Er with the values of various constants used in the calculations given elsewhere (Kumar and Chandra). The computed values of hyperfine (*hf*) parameters *A*, *B* and *P* are used to calculate  $C_M$ . Further,  $\langle \Delta E_Q \rangle_T$  is also computed in the range 10–400 K.

#### 4. Discussion

##### 4.1 Schottky specific heat

The Schottky specific heat (figure 1) for ErGaG shows two peaks unlike the Er<sup>3+</sup> : YAlG, which exhibits only one. The second peak in ErGaG appears due to the grouping of energy levels, because  $E_5^0$  is well separated ( $360.63 \text{ cm}^{-1}$ ) from  $E_1^0$  and this separation is much larger than crystal field splittings of Stark levels (in two groups) with  $i = 1 \rightarrow 4$  and  $i = 5 \rightarrow 8$  ( $65.45$  and  $77.87 \text{ cm}^{-1}$  respectively). On the other hand no such grouping exists in Er<sup>3+</sup> : YAlG. However, no experimental measurements are available for the comparison of these results. The extra entropy  $\Delta$  associated with the Schottky anomaly (table 2) for both the systems is in accordance with the doublet ground state free ion value obtained from the entropy expression  $S = R \ln (J + \frac{1}{2})$  to be  $17.3 \text{ J/g.at.wt. K}$ .

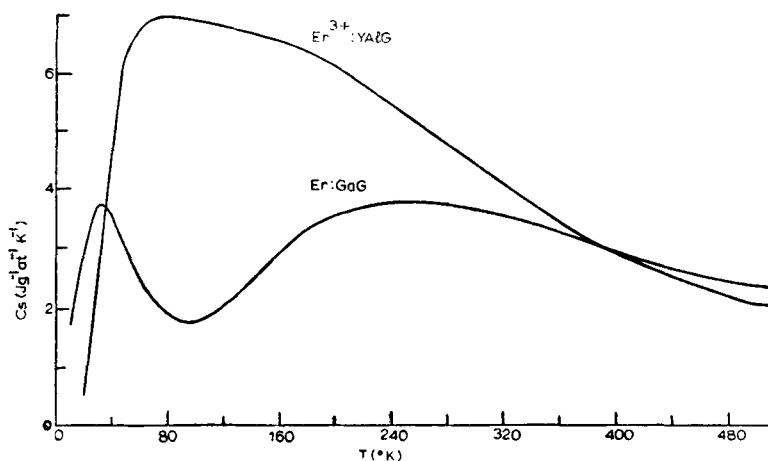
Figure 1. The curves for Schottky specific heat of ErGaG and Er<sup>3+</sup> : YAlG.

Table 2. Comparison of various calculated parameters with experimental data

Parameter		ErGaG	Er <sup>3+</sup> :YAIG
Schottky sp. heat	First peak		
	$T(K)$	30.0	70.0
	$C_s$	3.75	6.97
Second peak	$T(K)$	250.0	..
	$C_s$	3.86	..
Excess entropy	$S$ calc.	16.01	16.61
	theor.	17.29	17.29
Ground state $g$ factor	$g_{\parallel}$ calc.	6.565	0.903
	$g_{\perp}$ calc.	6.825	8.113
	$ \bar{g} $ calc.	6.738	5.710
	$ \bar{g} $ exp.	6.480 <sup>a</sup>	6.270 <sup>a</sup>
$\mu_{\text{eff}}$ (300 K) $\mu_B$	calc.	9.42	9.35
	exp.	9.52 <sup>b</sup>	9.52 <sup>b</sup>
$\mu_{\text{eff}}$ (0 K) $\mu_B$	calc.	5.85	5.85
	theor.	5.90 <sup>c</sup>	5.90 <sup>c</sup>
Curie constants	$C$ calc.	11.65	11.97
	exp.	11.98 <sup>d</sup>	11.98 <sup>d</sup>
	$\theta_p$ calc.	18.07	29.57

<sup>a</sup> Ball *et al* 1961; <sup>b</sup> Pop 1965; <sup>c</sup> Haman 1968; <sup>d</sup> Arajs and Miller 1960.

#### 4.2. The $g$ tensor

The computed values of  $g_{\parallel}$  and  $g_{\perp}$  for lowest Stark level in both the systems are listed in table 2. In the case of ErGaG,  $|\bar{g}| = 6.74$  compares well with the experimental value 6.48, obtained through PMR measurements by Ball *et al* (1961). On the other hand, for Er<sup>3+</sup>:YAIG the value of  $|\bar{g}| = 5.71$  is only in reasonable agreement with the experimental value 6.3 (Ball *et al* 1961). Further the sign of  $g$  tensor for the lowest levels is found to be positive in both the systems.

#### 4.3. The magnetic susceptibilities

The calculations of principal and mean magnetic susceptibilities for both systems show that  $K_{\perp} < K_{\parallel}$  throughout the temperature range 10–400 K (figures 2 and 3). From figure 2, it is clear that the calculated values of  $\bar{K}T$  as a function of temperature, for ErGaG are in good agreement with the experimental data of Ayant and Thomas (1963), in the range 10–300 K. Furthermore, the calculated results of  $\bar{K}T$  for Er<sup>3+</sup>:YAIG are in agreement with the experimental susceptibility data of Ball *et al* (1961) in the low temperature region. Further, a least square fit for the Curie Weiss law gives the values of constants as:

$$\text{ErGaG} \quad \bar{K} = 11.65/(T + 18.07)$$

$$\text{Er}^{3+}:\text{YAIG} \quad \bar{K} = 11.97/(T + 29.57).$$

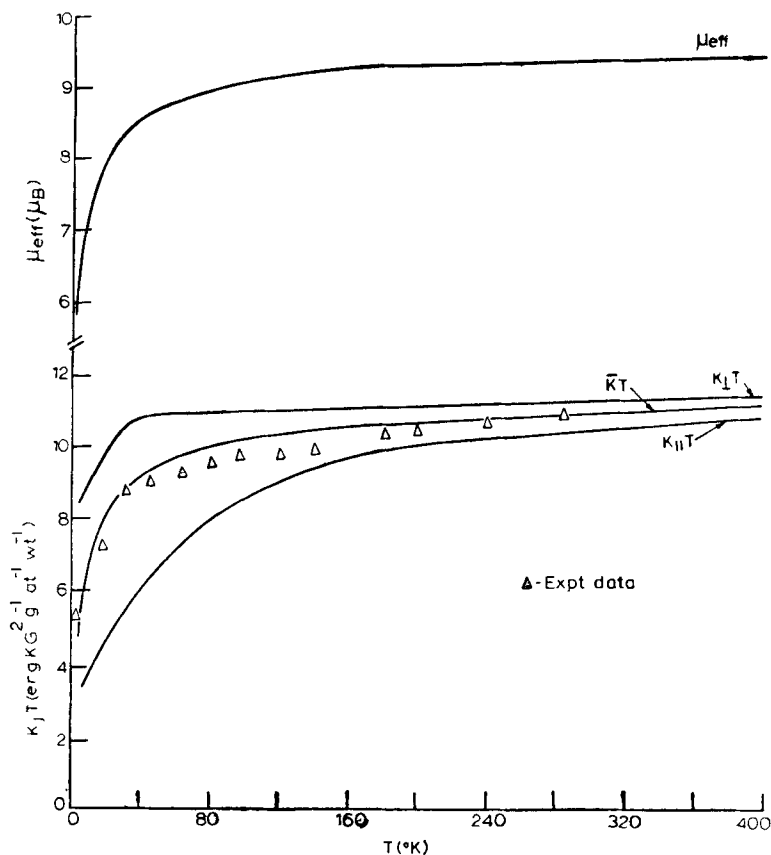


Figure 2. Temperature dependence of paramagnetic principal and mean susceptibilities of ErGaG.

It is further found that the magnetic anisotropy  $\Delta K$  increases continuously with the decrease of temperature (400–10 K) in both the systems.

#### 4.4. The effective magnetic moment

The temperature dependence of  $\mu_{\text{eff}}$  for ErGaG and  $\text{Er}^{3+}$ : YA1G is shown in figures 2 and 3. It is found that the value of  $\mu_{\text{eff}}$  does not change more than 3% from room temperature down to about  $T_3 = 90\text{K}$  for ErGaG and 120K for  $\text{Er}^{3+}$ : YA1G. Further the room temperature value of  $\mu_{\text{eff}}$  obtained for both the systems (table 2) is in good agreement with the value  $9.52 \mu_B$  obtained by Pop (1965) for Er. The extrapolated value of  $\mu_{\text{eff}}$  at OL (table 2) is also in good agreement with  $5.9 \mu_B$  value obtained by Hamann (1968).

#### 4.5. The hyperfine interactions

The calculated values of  $A$  and  $B$  of the hyperfine interaction tensor for  $^{166}\text{Er}$  and  $^{167}\text{Er}$  for both the systems are given in table 3. The sign of  $A$  in the present calculations is useful for Mossbauer studies whereas its magnitude in EPR

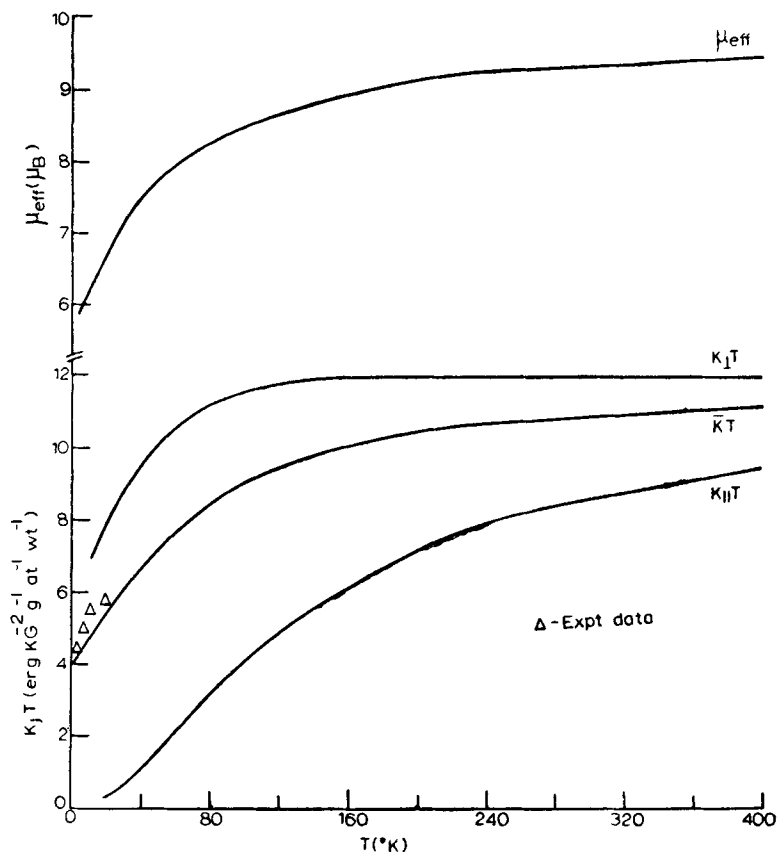
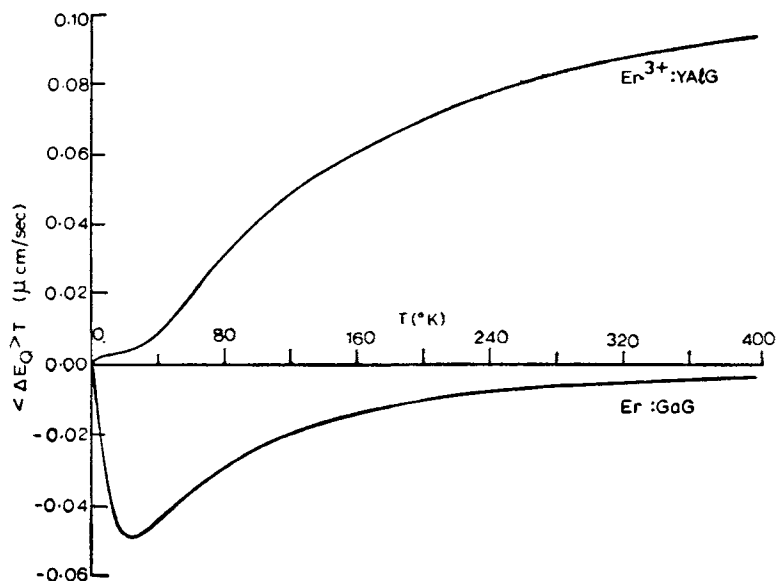


Figure 3. Temperature variation of paramagnetic principal and mean susceptibilities of Er<sup>3+</sup>:YAIG.

Table 3. Calculated hyperfine structure parameters of lowest Stark level for <sup>166</sup>Er and <sup>167</sup>Er, and the nuclear specific heat for <sup>167</sup>Er in garnets.

System	$A$	$B$	$P$	$C_M T^2$ (JK/g at wt)
ErGaG				
<sup>166</sup> Er	450.49	468.36	..	..
<sup>167</sup> Er	232.47	241.68	0.161	0.0386
Er <sup>3+</sup> :YAIG				
<sup>166</sup> Er	61.95	336.72	..	..
<sup>167</sup> Er	31.97	287.28	-0.446	0.0375

$A$ ,  $B$  and  $P$  are in units of  $10^{-4} \text{ cm}^{-1}$ .



**Figure 4.** The calculated quadrupole splitting for ErGaG and  $\text{Er}^{3+}:\text{YAIG}$  as a function of temperature.

measurements. In the absence of experimental data we are unable to compare the values of these parameters. The small value of  $P$ ,  $1.6 \times 10^{-5} \text{ cm}^{-1}$  for ErGaG and  $-4.66 \times 10^{-5} \text{ cm}^{-1}$  for  $\text{Er}^{3+}:\text{YAIG}$ , precludes its measurement by PMR experiments. Taking into account the natural abundance (22.94%) of  $^{167}\text{Er}$ , the contribution of hyperfine structure to specific heat at 1K is estimated to be  $3.86 \times 10^{-2}$  and  $3.75 \times 10^{-2} \text{ J/g.at.wt.K.}$ , for ErGaG and  $\text{Er}^{3+}:\text{YAIG}$  respectively.

The temperature dependence of quadrupole splitting  $\Delta E_Q$ , for  $^{166}\text{Er}$  (80.6 keV) in both the systems is shown in figure 4. To explain this variation we proceed with the assumption that with proper selection rule, there are two allowed Mossbauer transitions between the quadrupole split level (spin  $2^+$ ) and unsplit ground level (spin 0). Since the nuclear quadrupole moment of  $^{166}\text{Er}$  (80.6 keV) is negative, the negative value of  $\Delta E_Q$  for ErGaG suggests that  $\pm 1$  level with respect to '0' level is at lower energy, while a positive value of  $\Delta E_Q$  in  $\text{Er}^{3+}:\text{YAIG}$  should correspond to the higher energy of  $\pm 1$  level with respect to '0' level. However, single crystal Mossbauer measurements or magnetic perturbation experiments should be able to determine it more conclusively. The temperature dependent behaviour of  $\Delta E_Q$  can be understood in terms of the population of crystal field levels which influence the electric field at the nucleus. If we look, for example, to the two lowest Stark levels of  $\text{Er}^{3+}:\text{YAIG}$  and determine the effect of increased population of upper level due to increase of temperature it becomes evident from eq. (3), that  $\Delta E_Q$  should increase with temperature. This is because the lowest level contribution to  $\Delta E_Q$  is negative while that of the next higher level is positive. Similarly, the temperature dependence of ErGaG can also be explained on the same lines.

## 5. Conclusion

The increase in magnetic anisotropy with decrease in temperature and its high value at low temperatures is in conformity with the low symmetry of crystal field in these systems. Further, deviations from the predicted results can occur at low temperatures due to following reasons:

1. The crystal field parameters  $A_n^m \langle r^n \rangle$  are somewhat temperature-dependent.
2. The operator-equivalent coefficients  $\alpha_J$ ,  $\beta_J$  and  $\gamma_J$  depend on spin orbit parameter, which is always quenched by the host lattice interactions. Accordingly, these coefficients will be slightly different from the free ion values used in the present calculations.

However the satisfactory agreement of magnetic susceptibility,  $g$  values,  $\mu_{\text{eff}}$ , etc. for both the systems with corresponding experimental results, leads to the conclusion that the crystal field parameters used in the present calculations are reliably accurate. Therefore, the present analysis supports the hypothesis of Koningstein's, viz., main tetragonal crystalline fields in garnet systems.

## Acknowledgement

Two of the authors (VK and KC) wish to thank UGC, New Delhi for financial assistance to carry out this work.

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