

Magnetic Susceptibilities and Nuclear Hyperfine Properties of ErCl₃ Through Crystal Field Effects

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ABSTRACT

The present paper reports the magnetic susceptibility of powdered ErCl₃ at room temperature, and its thermal variation over a wide range of temperature using crystal field theory. The observed g-values of the diluted ErCl₃ were well explained with this theory. The nuclear hyperfine levels of ¹⁶⁶Er and ¹⁶⁷Er in ErCl₃ have also been determined. For ¹⁶⁶Er in ErCl₃, the expected Mössbauer transition lines were predicted. The hyperfine specific heat for ¹⁶⁷ErCl₃ has shown an inverse T² (where T represents temperature) rule in millikelvin temperature range.

1. Introduction

It has been observed that among the RE-crystals (having large number of 4f-electrons) Tb³⁺, Ho³⁺ and Dy³⁺ - crystals show magnetic ordering at liquid helium temperature. But Er³⁺ crystal such as Er(OH)₃, Er ethyl sulphate do not show any such ordering [1,2]. But magnetic susceptibility measurement at very low temperature (between 4K and 0.03K) shows a ferrimagnetic ordering [3] at about 0.307K. To analyse all these properties the ligand field produced by the neighboring chlorine anions is considered in the present paper. The free ion ground term of Er³⁺ is ⁴I_{15/2} followed by the first excited state ⁴I_{13/2} with energy separation of 6700 cm⁻¹. So the theoretical calculations considering only the ⁴I_{15/2} term would give accurate values of crystal field (CF) parameters and CF energy levels.

Earlier work on the measurement of g-values at low temperatures for its diluted sample [4] do not show any theoretical explanation. This study shows that value of g perpendicular to the symmetry axis C (8.832) for the sample is greater than g_{||} value (2.079 along parallel to the symmetry axis) i.e the sample is highly anisotropic. Again low temperature susceptibility measurement [3] reveals just opposite nature. To verify which of these above results is correct, we have adopted the problem and crystal field (CF) calculations have been done for magnetic, magneto-optical and nuclear hyperfine properties.

At low temperature the nuclear hyperfine properties of ¹⁶⁶Er and ¹⁶⁷Er in chloride crystal were also predicted by the theory.

2. Experimental

The average magnetic susceptibility of powdered ErCl₃ was measured at room temperature using Faraday Balance and its value was found to be (36430 ± 200) × 10⁻⁶ emu/mole.

3. Theoretical Considerations

ErCl₃ is a hexagonal compound where each Er³⁺ cation is surrounded by nine Cl⁻ anion [Fig.1]. The site symmetry of Er³⁺ ion in ErCl₃ is C_{3h}. When the ion sits in Chloride crystal structure its Hamiltonian becomes

$$H = H_{FI} + B_2^0 V_2^0 + B_4^0 V_4^0 + B_6^0 V_6^0 + B_6^6 (V_6^6 + V_6^{-6}) \quad \dots\dots\dots(1)$$

where H_{FI} represents free-ion Hamiltonian and the rest is that due to crystal field [5]. Operating by the Hamiltonian given in equation (1) on $|J, m_J\rangle$ basis states of Er³⁺ the CF energy levels and also the CF wavefunctions have been found out. Once the CF energy levels and corresponding wavefunctions are obtained, the values of magnetic susceptibilities along and perpendicular to symmetry axes were calculated using the Van-Vleck formula [6]. With the lowest eigenstate the g-values have also been calculated, which shows that g_⊥ >

g_{||}. By fitting the average susceptibility with the measured value at room temperature and calculated g-values with the experimental values [4] the appropriate set of CF parameters

B₂⁰, B₄⁰, B₆⁰ and B₆⁶ have been found out. Around 1K

and in millikelvin region, the specific heat of this type of RE solids arises due to Hyperfine interaction in the nucleus of RE³⁺ ion. The Hyperfine Hamiltonian H_{hf} is given by

$$H_{hf} = [A S_z I_z + B(S_x I_x + S_y I_y)] + P [3I_z^2 - I(I+1)]$$

$$\text{where } P = \frac{e^2 Q}{4I(2I-1)} \langle q_{zz} \rangle_T \quad \dots\dots\dots(2)$$

The term inside the first square bracket are due to nuclear magnetic hyperfine interaction, A and B are hyperfine constants, S is electronic spin and P is electric quadrupolar parameter. Generally in RE solids having a non-zero J value in the ground term, this term is more dominating. The crystalline electric field due to ligands produces an electric field gradient (EFG) at the nucleus. The second term of eq (2) is the product of EFG i.e $\langle q_{zz} \rangle_T$ and the nuclear quadrupole moment Q. EFG has two parts i.e lattice and 4f electronic part.

$$\langle q_{zz} \rangle_T = (1 - \gamma_\infty) q_{zz}^{(latt)} + (1 - R_Q) \langle q_{zz} \rangle_T^{4f} \quad \dots\dots\dots(3)$$

where γ_∞ and R_Q are lattice and atomic Sternheimer factors. For RE ion in static crystalline field the lattice contribution of EFG i.e q_{zz}^{latt} is considered to be temperature independent however the 4f electronic part of EFG i.e $\langle q_{zz} \rangle_T^{4f}$ is dependent on temperature. The thermal average of EFG is associated with CF energy values (E_ψ) and CF wave function (ψ) as

$$\langle q_{zz} \rangle_T^{4f} = \frac{\sum_{\psi=1}^{2J+1} \langle \psi | q_{zz}^{4f} | \psi \rangle \exp(-\frac{E_\psi}{k_B T})}{\sum_{\psi=1}^{2J+1} \exp(-\frac{E_\psi}{k_B T})}$$

$$\langle \psi | q_{zz}^{4f} | \psi \rangle = -\langle J || \alpha || J \rangle \langle r^{-3} \rangle_{4f} \langle \psi | 3J_z^2 - J(J+1) | \psi \rangle \dots\dots\dots (4)$$

Here $\langle J || \alpha || J \rangle$ is operator equivalent to the hyperfine interaction. Similarly the lattice contribution of the EFG is related to the crystalline electric field as follows

$$q_{zz}^{(latt)} = -\frac{4B_2^0[(1-\gamma_\alpha)/(1-\sigma_2)]}{e^2 \langle r^2 \rangle_{4f}} \dots$$

(5) Here B_2^0 is the CF parameter which was accurately obtained from magnetic measurement [1,2]. The other constants values were taken from Ref. [7 – 9].

4. Results and Discussion

4.1 Magnetic Susceptibility and g-values

The thermal variation of magnetic susceptibility along parallel ($K_{||}$) and perpendicular(K_{\perp}) direction of symmetry axis and their anisotropy ($\Delta K = K_{\perp} - K_{||}$) were calculated over wide range of temperatures (between 300K and 10K). At room temperature the mean magnetic susceptibility was found to be 36430×10^{-6} emu/mole whereas the best fitted results give as 36289×10^{-6} emu/mole. The accurate set of CF parameters (in cm^{-1}), crystal quantum number(μ), energy levels (in cm^{-1}) and wavefunctions are given in Table-1 .

Table 1 CF energy levels and CF wavefunctions of the sample

$$B_2^0 = 75, B_4^0 = -43, B_6^0 = -41, B_6^6 = 540(cm^{-1})$$

μ	Energy levels (cm^{-1})	Wavefunctions
$\frac{5}{2}$	-199.39	$0.749 \left \pm \frac{7}{2} \right\rangle - 0.662 \left \mp \frac{5}{2} \right\rangle$
$\frac{3}{2}$	-172.81	$0.234 \left \pm \frac{15}{2} \right\rangle - 0.744 \left \pm \frac{3}{2} \right\rangle + 0.626 \left \mp \frac{9}{2} \right\rangle$
$\frac{3}{2}$	-17.90	$-0.967 \left \pm \frac{15}{2} \right\rangle - 0.096 \left \pm \frac{3}{2} \right\rangle + 0.235 \left \mp \frac{9}{2} \right\rangle$

$\frac{1}{2}$	18.37	$-0.222 \left \pm \frac{13}{2} \right\rangle + 0.811 \left \pm \frac{1}{2} \right\rangle - 0.542 \left \mp \frac{11}{2} \right\rangle$
$\frac{1}{2}$	36.18	$-0.409 \left \pm \frac{13}{2} \right\rangle + 0.193 \left \pm \frac{1}{2} \right\rangle + 0.892 \left \mp \frac{11}{2} \right\rangle$
$\frac{5}{2}$	44.58	$0.662 \left \pm \frac{7}{2} \right\rangle + 0.749 \left \mp \frac{5}{2} \right\rangle$
$\frac{3}{2}$	63.49	$0.129 \left \pm \frac{15}{2} \right\rangle + 0.703 \left \pm \frac{3}{2} \right\rangle + 0.699 \left \mp \frac{9}{2} \right\rangle$
$\frac{1}{2}$	227.47	$0.719 \left \pm \frac{13}{2} \right\rangle + 0.565 \left \pm \frac{1}{2} \right\rangle + 0.403 \left \mp \frac{11}{2} \right\rangle$

The magnetic anisotropy is 7002×10^{-6} emu/mole at 300K which is 19% to the average value at room temperature. At Room temperature $K_{||} < K_{\perp}$ since the Er^{3+} ions are far away along c axis than along a axis. Both of them follow the Curie-Weiss law down to some specific temperature as follows

$$K_{||} = \frac{11.887}{T - 89.152} \quad (\text{down to 120K})$$

$$K_{\perp} = \frac{11.333}{T + 3.400} \quad (\text{down to 40K})$$

$$\bar{K} = \frac{11.666}{T - 23.333} \quad (\text{down to 60K})$$

..... (6)

The Curie constants are nearly same and very close to that of free ion value i.e 11.435 emu/mole but the Weiss constants are different due to anisotropic magnetic properties. The thermal variation of $K_{||}$, K_{\perp} , \bar{K} and ΔK are shown graphically in the Fig. 2.The experimental and theoretical g-values are given in Table 2. Both the results justify that magnetic and magneto-optical properties are larger along a-axis than along c-axis. Similar behaviour have been found for other Er^{3+} compounds [1,8,9]

Table 2 g-values of $ErCl_3$ and its diluted salt

Sample	$g_{ }$	g_{\perp}	Ref
$Er^{3+}:LaCl_3$	1.989 ± 0.001	8.757 ± 0.001	Hutchison and Wong (1958).[4]
$ErCl_3$	2.079	8.832	Present Work

4.2 Nuclear Hyperfine properties

Operating H_{hf} on basis state $|I, m_I\rangle$, HF energy levels for ground($I_g=7/2$) and first excited($I_e=9/2$) state for ^{167}Er were determined. From Ref [1,8,9] using $A/g_{||}$ and B/g_{\perp} values for various Er^{3+} compounds and substituting g- values of the present work (Table-2) the hyperfine constants A and B were found to be $71.99 \times 10^{-4} cm^{-1}$ and $310.5 \times 10^{-4} cm^{-1}$ respectively. The nuclear ground term of

¹⁶⁷Er (*I_g*=7/2) is followed by the first excited term (*I_e*=9/2) at 79.32 KeV above. The EFG for 4f-electronic part was calculated using the CF energy levels and wavefunctions (Table-1) and its thermal variation is shown in Fig.3 .

The value of EFG becomes nearly constant below 5K. Taking the temperature-dependent and temperature-independent part of EFG , the value of electric quadrupole parameter for both ground (*P_g*) and first excited state (*P_e*) were computed. Both of them become temperature-independent at about 5 mK (Fig.4) .

Using the values of A, B and P the hyperfine levels were calculated. Due to hyperfine interaction *I_g* (=7/2) with effective spin (*S*=1/2) splits into 7 doublets and 2 singlets with total width ~ 0.1242 cm⁻¹. The first excited state *I_e* (=9/2) splits into 9 doublets and 2 singlets with total width~ 0.1550 cm⁻¹ (Fig-5). Here the eigen states corresponding to these levels are not pure $|m_l\rangle$ states but are single or combination of $|m_l, m_s\rangle$ states.

The HF specific heat was calculated using the following formula [11]

$$C_{hf} = \frac{Nk_B}{Z^2} [Z \sum_{i=1}^m X_i^2 \exp(-X_i) - \{ \sum_{i=1}^m X_i \exp(-X_i) \}^2]$$

where $X_i = \frac{E_i^{(0)}}{k_B T}$ and Z = partition function here

E_i⁽⁰⁾ represents energy values of the HF split levels of nuclear ground state. Its value gives two peaks at 1.2 mK and 54.5 mK with magnitude 0.765R and 0.567R respectively. It also varies as 1/*T*² (where *T* represents absolute temperature) over a large temperature range (between approximately 250 mK and 1K). The nature of *C_{hf}* is shown in the Fig. 6 .

No direct experiments on Mössbauer spectroscopy have been performed for ErCl₃ containing ¹⁶⁷Er. We have studied the nuclear properties of ¹⁶⁶Er in ErCl₃ as the work have been done for ¹⁶⁶Er in Er(OH)₃ [Ref-7]. The hyperfine structure of ¹⁶⁶Er in ErCl₃ was calculated. For ¹⁶⁶Er nucleus the nuclear ground term has *I_g*=0 so there is no hyperfine splitting. But first excited term (80.6 KeV above the ground term) has *I_e*=2 which gives fine structures. Its *P_{ex}* was found to be 3.698×10⁻⁴ cm⁻¹ at and below 5 mK . The lattice and 4f electronic part of the field gradient were taken as obtained for ¹⁶⁷Er in ErCl₃ . The value of Q (quadrupole moment of the nucleus) was altered accordingly. The result has been shown in Fig.7 with the possible Mossbauer transition using the condition of dipolar transition i.e $\Delta m_l = 0, \pm 1$. Four lines are obtained for this sample.

5. Conclusions

ErCl₃ is a strong paramagnetic compound with \bar{K} as 36289×10⁻⁶ emu/mole. From the values of *K_{||}* and *K_⊥* (where *K_{||}* < *K_⊥*) we found that this sample is also

highly anisotropic at RT. On cooling this anisotropy increases more rapidly than the average property so that at 80K the percentage on average property becomes 89% because the *K_⊥* component increases at faster rate than *K_{||}* owing to crystal field. Again from measurement of g-values it has been observed that *g_{||}* > *g_⊥* . All these results reveal that the Er³⁺ ions are closely spaced along a-axis than along c-axis. But magnetic study at very low temperature [3] gives completely different results. It may be due to the fact that at about 0.3K temperature a structural second order phase change occurs in the crystal. In some Nd3+ -crystal (which is the mirror RE element of Er) such structural change has been observed [2] .

In crystal like ErCl₃ in which the CF parameters do not change with temperature it is possible to calculate some important hyperfine properties at millikelvin temperature range . Here the hyperfine constants A and B are found to be proportional to *g_{||}* and *g_⊥* respectively and B is greater than A . Since *C_{hf}* depends on only *B₂*⁰ it can be determined from *C_{hf}* measurement. As *C_{hf}* obeys inverse *T*² law at millikelvin range this property can be utilized for millikelvin thermometry. Mössbauer and other HF experiments are welcome for the sample specially at about 4K to verify whether a second order structural phase change occurs inside the crystal or not .

Figures and figure captions

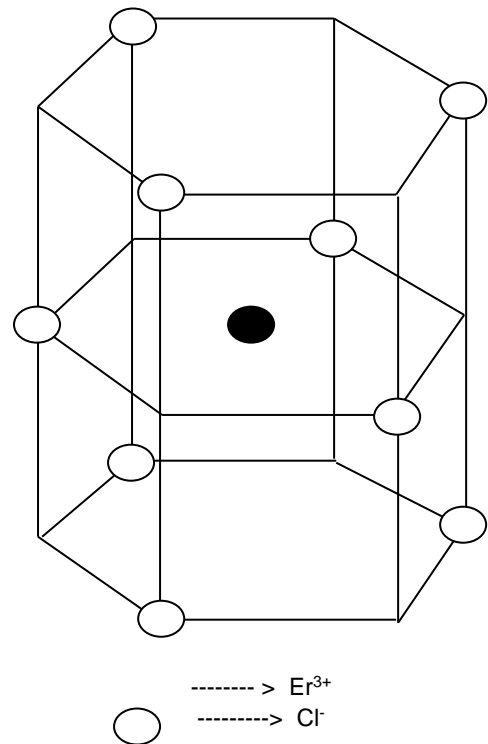


Fig.1 Structure of ErCl₃ unit cell (not in scale)

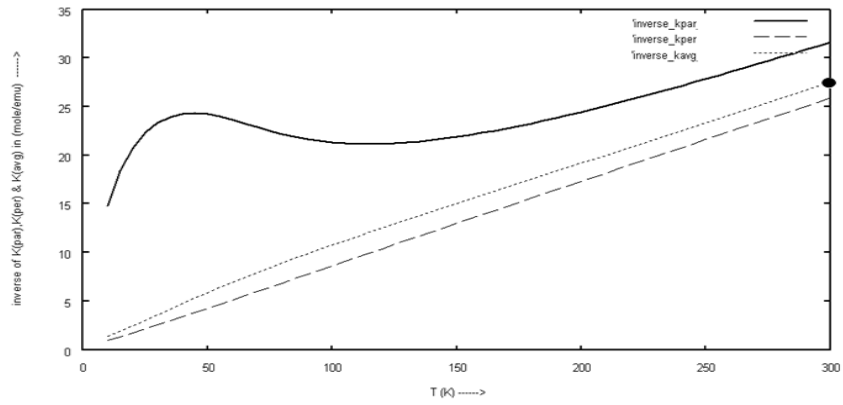


Fig.2(a) Thermal variation of $(1/K_{||}), (1/K_{\perp})$ and $(1/\bar{K})$; ● ' represents the experimental value

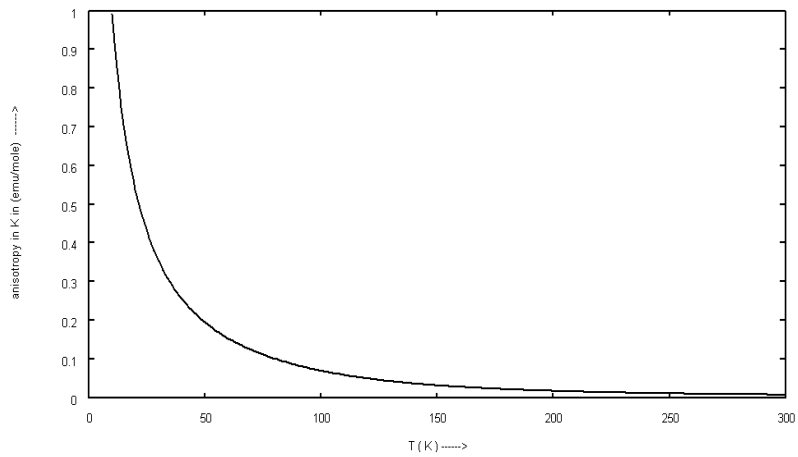


Fig.2(b) Thermal variation of anisotropy ΔK

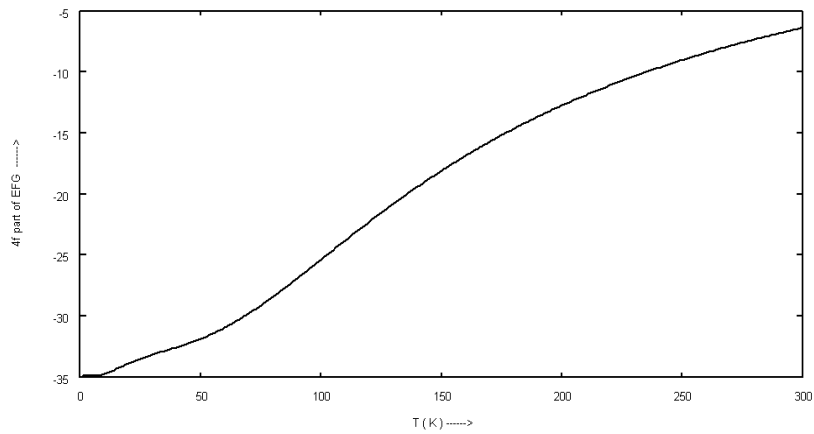


Fig.3 Thermal variation of 4f part of (EFG)

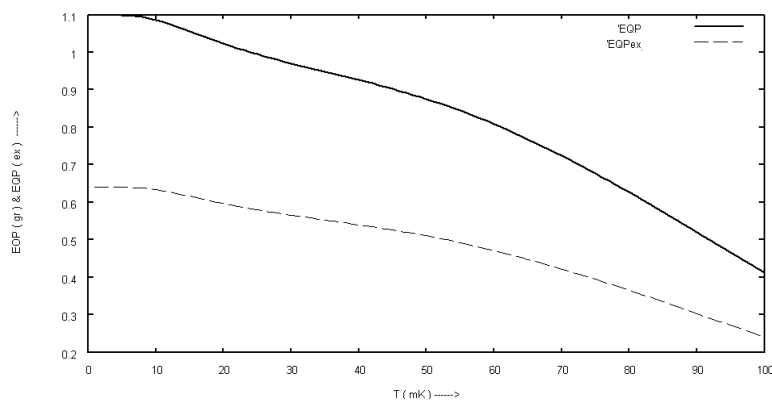


Fig.4 Thermal variation of $P_{gr}(\text{---})$ and $P_{ex}(\text{- - - - -})$

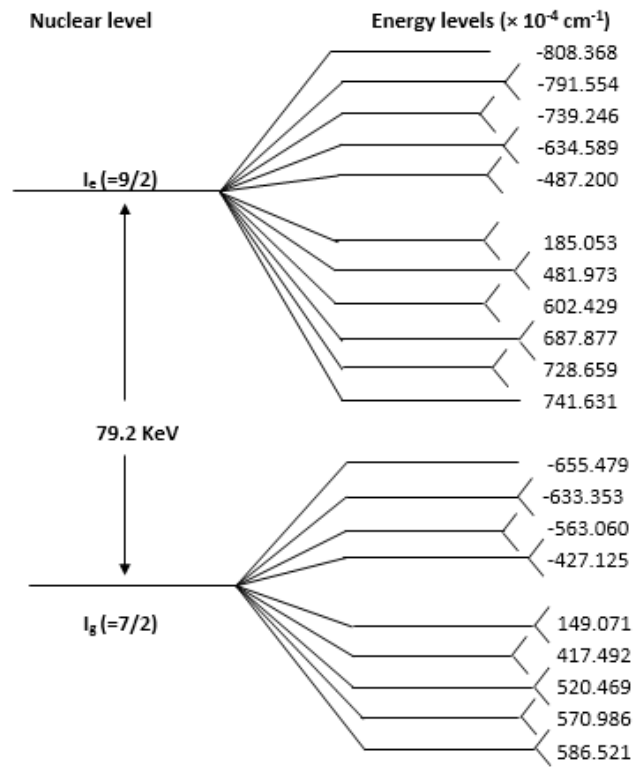


Fig.5 HF energy levels for $^{167}\text{ErCl}_3$ (not in scale)

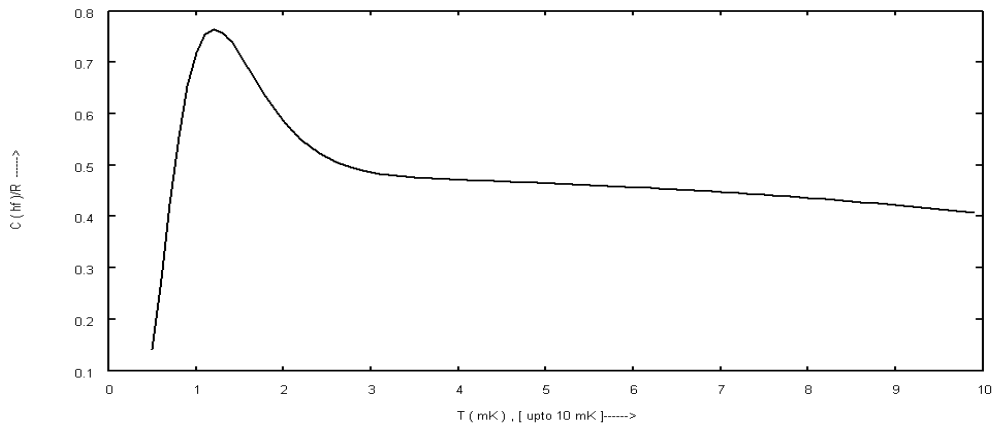


Fig .6(a) Thermal variation of hyperfine specific heat (upto10 mK)

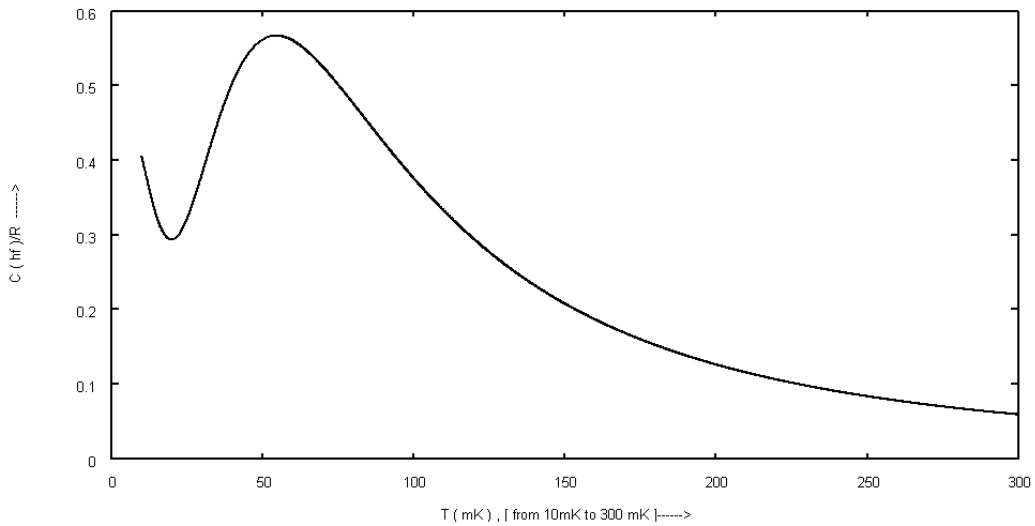


Fig .6(b) Thermal variation of hyperfine specific heat (from 10mK to 300 mK)

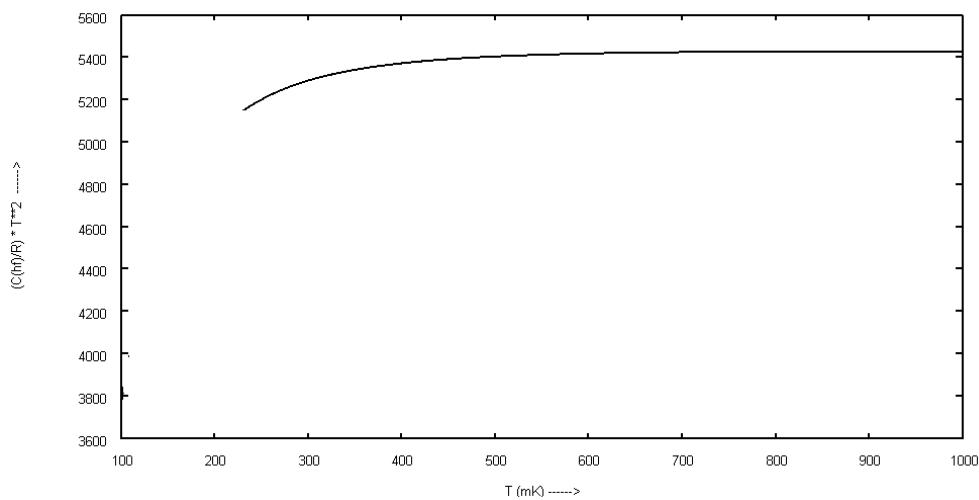


Fig.6(c) Thermal variation of $[C(hf)/R] \times T^2$ (in mK^2)

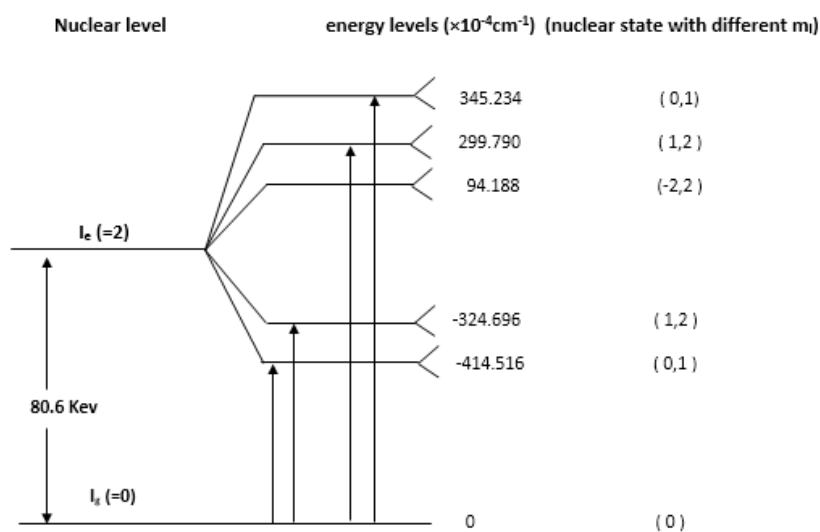


Fig.7 Mössbauer transition for $^{166}ErCl_3$

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