

Nuclear Hyperfine Properties of Potassium Neodymium Fluoride (KNd₃F₁₀) Through Crystal Field Effects

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Abstract:- The present paper reports the nuclear hyperfine properties of KNd₃F₁₀ with the help of crystal field theory after finding the crystal field parameters which are essential for the aforesaid properties . The observed g-values of the sample were well explained with this theory with the comparison with some other samples. The nuclear hyperfine levels of ¹⁴³Nd has been determined . The hyperfine specific heat for KNd₃F₁₀ has shown an inverse T² (where T represents temperature) rule in millikelvin temperature range.

Keywords:- Crystal Field Effect, G-Values, Hyperfine Interaction, Hyperfine Specific Heat.

I. INTRODUCTION

For rare earth family very few studies on Nd³⁺ compounds had been made as it is most abandoned unlike highly magnetic Er³⁺ compounds. A Magnetic study on NdES [1] has shown that the ground term splitting is 308 cm⁻¹ with |±5/2> as ground state . Again magnetic and EPR studies on some other Nd³⁺ compounds furnish that $g_{\perp} < g_{\parallel}$. Recently magnetic susceptibility measurements have been done on potassium erbium fluoride (KEr₃F₁₀) by Chamberlein and Corruccini [4] at low temperatures . Again a detailed magnetic study have been done on KEu₃F₁₀ by Bhattacharyya [3] and KPr₃F₁₀ theoretically very recently [7] . Similar study on KNd₃F₁₀ has been made keeping all the aforesaid information in mind using crystal field theory [9]. Hence in the present paper we report the nuclear hyperfine properties of KNd₃F₁₀.

II. THEORETICAL CONSIDERATIONS

KNd₃F₁₀ has tetragonal structure having site symmetry C_{4v} for Nd³⁺ ion. Operating by the Hamiltonian obtained from crystal field effects given on |J, m_J> basis states of Nd³⁺ the CF energy levels and also the CF wavefunctions have been found out with the eigenstate |±5/2> as ground state and ground term splitting nearly 317 cm⁻¹ . Once the CF energy levels and corresponding wavefunctions are obtained, g values along symmetry axis and perpendicular to that were calculated which shows that $g_{\perp} < g_{\parallel}$ by fitting the appropriate set of CF parameters B₂⁰, B₄⁰, B₆⁰ ,

B₆⁴ and B₄⁴ The Hyperfine Hamiltonian H_{hf} is given by $H_{hf} = [AS_z I_z + B(S_x I_x + S_y I_y)] + P [3I_z^2 - I(I+1)]$ where $P = \frac{e^2 Q}{4I(2I-1)} \langle q_{zz} \rangle_T$ (1)

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.

$$\langle q_{zz} \rangle_T = (1 - \gamma_{\infty}) q_{zz}^{(latt)} + (1 - R_Q) \langle q_{zz} \rangle_T^{4f} \dots\dots\dots(2)$$

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

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

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

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;

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

Here B_2^0 is the CF parameter which was accurately obtained from theoretical calculation [9] and also other constants were calculated accordingly.

III. RESULTS AND DISCUSSION

3.1 The set of CF parameters (in cm^{-1}), energy levels (in cm^{-1}) and wavefunctions are given in Table-1 .

Table 1 CF energy levels and CF wavefunctions of the sample

Energy levels	Wave functions
-103.13	$0.996 \left \pm \frac{5}{2} \right\rangle - 0.085 \left \mp \frac{3}{2} \right\rangle$
-85.889	$0.267 \left \pm \frac{9}{2} \right\rangle - 0.818 \left \mp \frac{1}{2} \right\rangle + 0.509 \left \pm \frac{7}{2} \right\rangle$
-56.962	$-0.866 \left \pm \frac{9}{2} \right\rangle + 0.368 \left \pm \frac{1}{2} \right\rangle + 0.338 \left \mp \frac{7}{2} \right\rangle$
31.663	$0.085 \left \pm \frac{5}{2} \right\rangle + 0.996 \left \mp \frac{3}{2} \right\rangle$
214.32	$0.434 \left \pm \frac{9}{2} \right\rangle + 0.896 \left \pm \frac{1}{2} \right\rangle - 0.096 \left \mp \frac{7}{2} \right\rangle$

The most appropriate CF parameters are $B_2^0 = 96, B_4^0 = -270, B_6^0 = -1, B_4^4 = 5, B_6^4 = -240$

Table 2 g-values of different Nd- Compounds :-

Sample	Symmetry	$g_{ }$	g_{\perp}	Ref
NdES	C_{3h}	3.594	2.039	Nath & Ghosh,1982 [1]
NdCl ₃	C_{3h}	3.444	2.277	Bhattacharya et al, 2015 [8]
KNd ₃ F ₁₀	C_{4v}	3.594	1.132	Bhattacharya 2019 [9]

3.2 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 ¹⁴³Nd were determined. From Ref [5] using the value of constant A and $g_{||}$ from ref [9] calculating $A/g_{||}$ and

B/g_{\perp} values for various Nd³⁺ compounds and substituting g- values of the present work (Table-2) the hyperfine constants A and B were found to be $67.0 \times 10^{-4} \text{ cm}^{-1}$ and $21.1 \times 10^{-4} \text{ cm}^{-1}$ respectively. The nuclear ground term of ¹⁴³Nd ($I_g=7/2$) is followed by the first excited term ($I_e=9/2$) at few 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.1.

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 10 mK (Fig.2) . 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 ~ 0.0328 cm^{-1} . The first excited state $I_e (=9/2)$ splits into 9 doublets and 2 singlets with total width~ 0.0305 cm^{-1} (Fig-3). Here the eigen states corresponding to these levels are not pure $|m_I\rangle$ states but are single or combination of $|m_I, m_S\rangle$ states.

The HF specific heat was calculated using the following formula [2]

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

where $X_i = \frac{E_i^{(0)}}{k_B T}$ and Z = partition function(5)

Here $E_i^{(0)}$ represents energy values of the HF split levels of nuclear ground state. Its value gives one peak at 6.9 mK with magnitude 0.9609R respectively (Fig. 4). It also varies as $1/T^2$ (where T represents absolute temperature) over a large temperature range (between approximately 100 mK and 5K , Fig. 5)

IV. CONCLUSIONS

In crystal like KNd₃F₁₀ 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_{\perp} respectively and A is greater than B . Since q_{zz}^{latt} depends on only B_2^0 only the values of C_{hf} at different temperatures can be determined using corresponding formula [5] . As C_{hf} obeys inverse T² law at millikelvin range i.e these values remain nearly constant of approximate value 158 mK^2 (Fig. 5) near to 100mK , this property can be utilized for millikelvin thermometry.

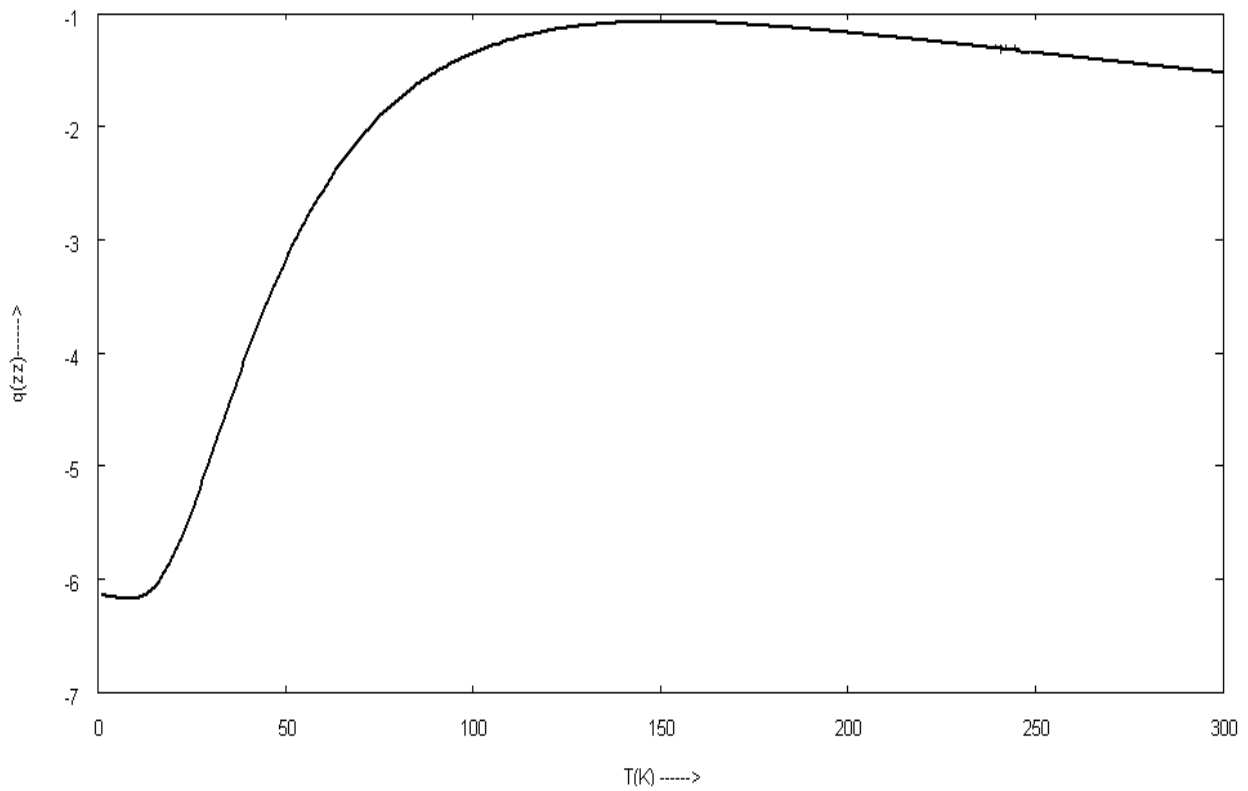


Fig.1 Thermal variation of 4f part of (EFG)

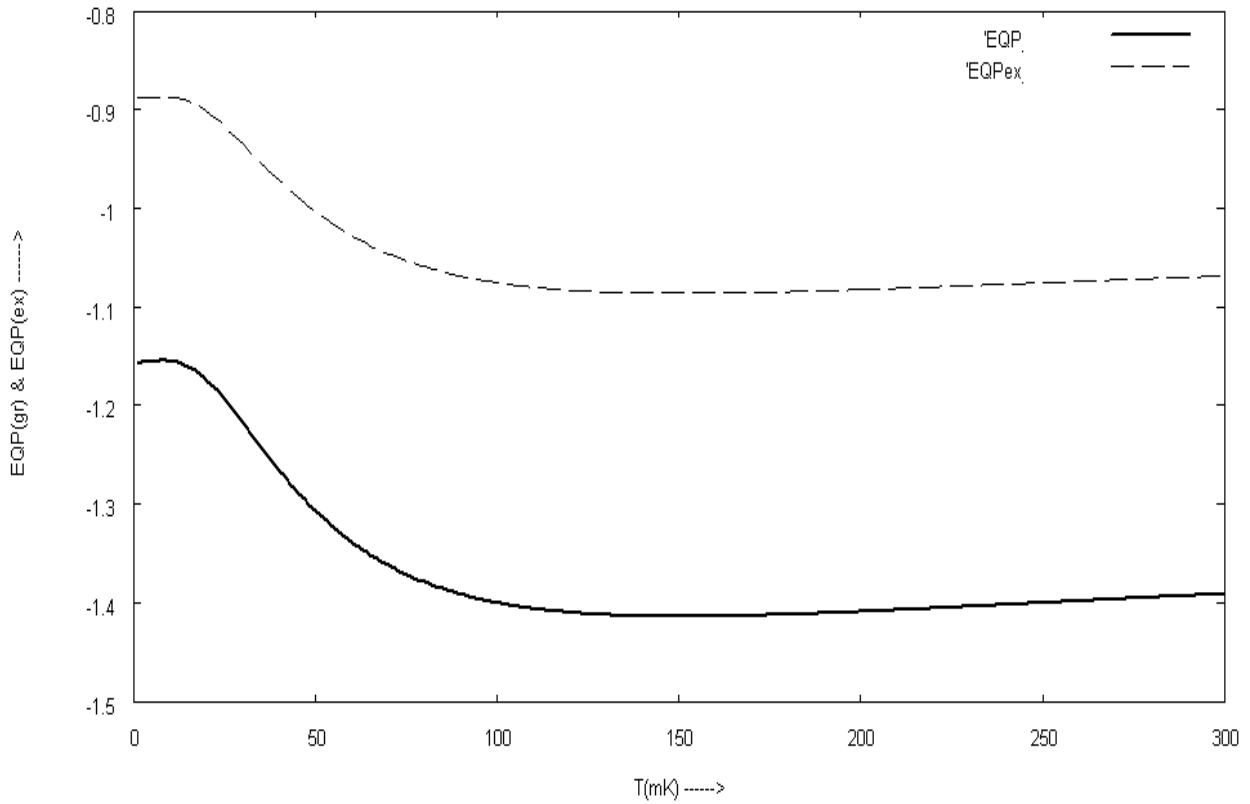


Fig.2 Thermal variation of P_{gr} (——) and P_{ex} (- - - -)

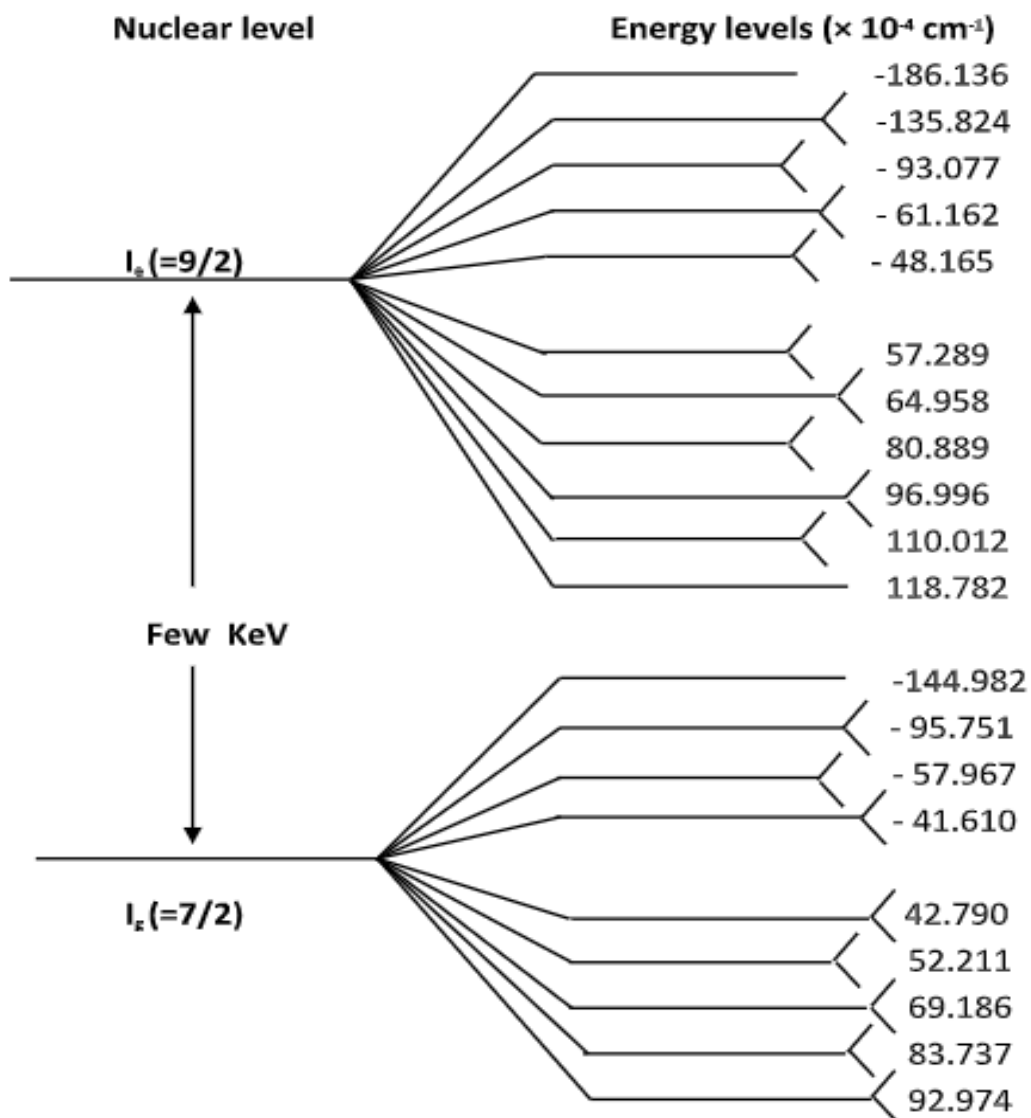


Fig.3 HF energy levels for $K^{143}NdF_{10}$ (not in scale)

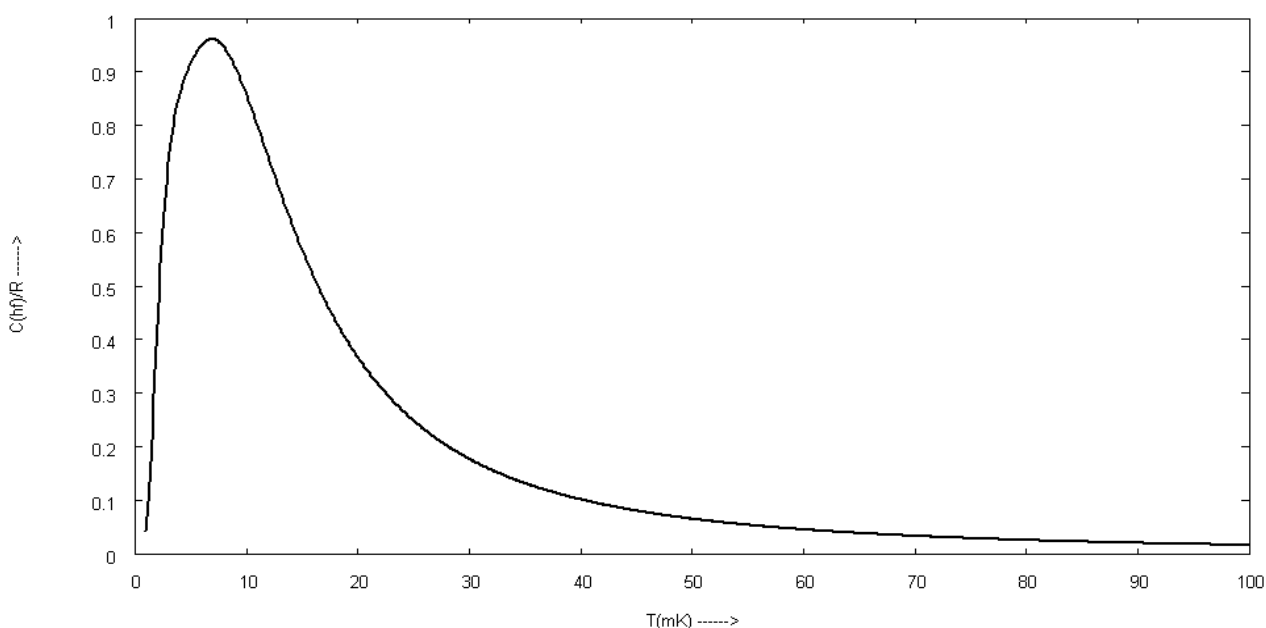


Fig .4 Thermal variation of hyperfine specific heat

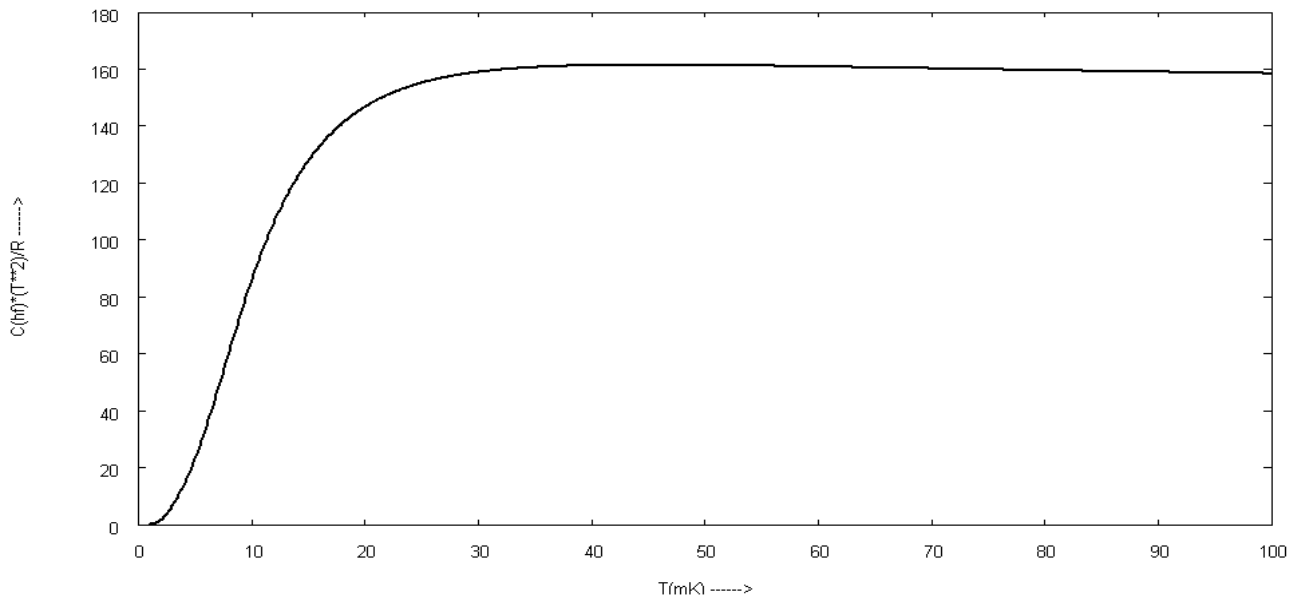


Fig. 5 Thermal variation of $[C(hf)/R] \times T^2$ (in mK^2)

REFERENCES

- [1]. Nath A , Ghosh U.S ,Phys. Stat.Sol.(b)112, 187 (1982)
- [2]. S.Dasgupta,M.Saha and D.Ghosh ,J.Phys.Chem.Solids.45,589 (1984)
- [3]. Bhattacharyya S , J. Appl .Phys 80 , 5213 (1996)
- [4]. Chamberlein S.L and Corruccini L.R , Phys Rev B 71 , 024434 (2005)
- [5]. Hong Liang Ma , Chin.Phys , 14 (3) , 511 (2005)
- [6]. Roy S , Thesis “ Magnetic , Optical and Nuclear Hyperfine properties of Some Praseodymium and Thulium Compounds” (2009) , Unpublished
- [7]. Bhattacharya S & Bhattacharyya S, Research Hub(RHIMRJ),2,issue 1,1-5(2015)
- [8]. Bhattacharya S , Research review journals,4,issue-02, 1733-35 (2019)