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Research Paper

Thermal Variation of Different Components of Specific Heat for $ErCl_3$

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Abstract: ***This paper reports the thermal variation of different specific heat components and entropy of*** $ErCl_3$***. The lattice component was calculated by adopting the empirical formula given by Chirico and Westrum (1980). The Schottky component was calculated between 10K and 300K using the crystal field energy levels . The hyperfine splitting of*** ^{167}Er ***in*** $ErCl_3$ ***was found to be ~*** 1240×10^{-4} cm^{-1} ***and with these split energy levels the hyperfine specific heat was calculated . Two peaks were observed in its thermal variation . These peaks are 0.765R and 0.567R at about 1.2mK and 54.5mK respectively.***

Key Words: Crystal field effect, Schottky specific heat, Hyperfine interaction.

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1. Introduction

Rare Earth (RE) hydroxides having large number of 4f-electron (i.e Tb^{3+},Ho^{3+},Dy^{3+}) the show magnetic ordering at about 4K. But $Er(OH)_3$ does not show any such ordering. Whereas $ErCl_3$ revealed a ferrimagnetic ordering anomaly at much lower temperature (T_C=0.307K) studied by Fairall et al (1971) [1] . Since the present paper reports the thermal variation of different specific heat components down to 10K (except for hyperfine specific heat) , we consider only the ligand field produced nine Cl^- ions surrounding the Er^{3+} ion for this study. In $ErCl_3$ crystal the site symmetry of Er^{3+} ion is C_{3h} .

The ground term of Er^{3+} ion is $^4I_{15/2}$ followed by first excited state $^4I_{13/2}$ with energy gap 6700 cm^{-1}. So consideration of crystal field (CF) theory will be preferred for theoretical calculation to evaluate the CF parameters and CF energy levels to match the experimentally obtained g-values [2] . From these value of CF energy levels the thermal variation of Schottky specific heat was evaluated over a wide range of temperature.

The calculation of lattice specific heat was done using the empirical formula given by Chirico and Westrum[3] and with the corresponding values of lattice specific heat obtained for $LaCl_3$ and $GdCl_3$ [4]. At millikelvin temperature region the thermal variation of nuclear hyperfine specific heat was also estimated and it shows the inverse T^2 law , where T represents absolute temperature, over a certain temperature range.

2. Theoretical considerations

The total specific heat C_T of the $ErCl_3$ crystal can be expressed as

$$C_T = C_L + C_{sh} + C_M + C_{hf} \quad \ldots\ldots\ldots\ldots (1)$$

where C_L Is lattice specific heat, C_{sh} is Schottky specific heat, C_M is magnetic specific heat and C_{hf} is nuclear hyperfine specific heat. The last two terms i.e C_M and C_{hf} are important below 1K. Chirico and Westrum [2] gave an empirical interpolation formula to find out the values of C_L for both RE-hydroxides and RE-trichlorides as follows

$$C_L\{LnCl_3\}=(1-f)\{C_L\{LaCl_3\}\}+f[C_L\{GdCl_3\}] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where the f-factor is related to the molar volume (V) of $LaCl_3$, $GdCl_3$ and $LnCl_3$ according to the following relation

$$f\{LnCl_3\} = \frac{V\{LnCl_3\} - V\{LaCl_3\}}{V\{GdCl_3\} - V\{LaCl_3\}} \quad \ldots\ldots\ldots\ldots (3)$$

Between 10K and 300K as CF effects play the most important role in the solid , C_{sh} becomes interesting. Its thermal variation was calculated using CF energy levels with the formula [5] :

$$C_{sh} = \frac{Nk_B}{Z^2}[Z\sum_{i=1}^{m} X_i^2 \exp(-X_i) - \{\sum_{i=1}^{m} X_i \exp(-X_i)\}^2] \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where $X_i=E_i^{(0)}/k_BT$ and Z = partition function here $E_i^{(0)}$ represents the CF energy levels .

For the sample the total entropy has been computed over a wide range of temperatures .

The ^{167}Er (having nuclear spin I_g=7/2) and quadrupole moment Q interacting with electric field gradient (EFG) produced by CF effects of neighbouring chloride ions will cause the splitting of nuclear levels. The nuclear specific heat was calculated in millikelvin temperature range. The hyperfine Hamiltonian is given by

$$H_{hf} = [\,AI_zS_z + B\,(I_xS_x+I_yS_y)\,] + P[3I_z^2-I(I+1)] \qquad \ldots\ldots\ldots\ldots\ldots \qquad (5)$$

$$\text{where} \quad P = \frac{e^2Q}{4I(2I-1)}\langle q_{zz}\rangle_T \qquad \ldots\ldots\ldots\ldots\ldots \qquad (6)$$

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 interaction parameter (EQP) . The crystalline electric field due to ligands produces an EFG at the nucleus. The second term of eq-5 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.

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

(7) where γ_∞ and R_Q are lattice and atomic Sternheimer factors.. The thermal average of EFG is associated with CF energy values (E_ψ) and CF wavefunction (ψ) as

$$\langle q_{zz}\rangle_T^{4f} = \frac{\sum_{\psi=1}^{2J+1}\langle\psi|q_{zz}^{4f}|\psi\rangle\exp(-\frac{E_\psi}{k_BT})}{\sum_{\psi=1}^{2J+1}\exp(-\frac{E_\psi}{k_BT})} \quad \text{and} \quad \langle\psi|q_{zz}^{4f}|\psi\rangle = -\langle J\|\alpha\|J\rangle\langle r^{-3}\rangle_{4f}\langle\psi|3J_z^2-J(J+1)|\psi\rangle$$

…………… (8 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

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

………………. (9)

Here B_2^0 is the first CF parameter which was accurately obtained from magnetic studies. The other nuclear constant values were taken from Ref. [6 – 8]. Operating by H_{hf} on basis state $|I, m_I\rangle$ the HF energy levels for ground state as well as for first excited state (I_e=9/2) for ^{167}Er were determined. The thermal variation of C_{hf} was calculated using equation(4) with the aid of the hyperfine split energy levels.

3. Results and discussions

With the help of crystal field theory we have determined the crystal field energy levels and the corresponding wavefunctions of $ErCl_3$. These are given in Table 1.

Table 1 CF parameters (in cm^{-1}) , B_2^0=75, B_4^0=-43, B_6^0=-41, B_6^6=540

CF energy levels and CF wavefunctions of the sample

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 factor ‘f’ for different RE-chlorides have been calculated and are shown in Fig-1 with the number of different 4f-electrons. For $ErCl_3$ the value of f was found to be 1.38 .

The values of lattice and Schottky specific heat and entropy (S) at different temperatures for this sample are given in the following table . The thermal variation of C_L and C_{sh} are shown in Fig 2(a) & 2(b) .

Table-2 Thermal nature of lattice and Scottky specific heat and entropy

T (K)	C_L/R	C_{sh}/R	S/R
10	0.174	0.304	0.371
15	0.644	0.437	0.662
40	4.284	0.264	2.318
80	12.128	0.771	6.088
100	14.963	0.929	7.903
115	16.602	0.956	9.214
120	17.030	0.953	9.506
150	19.188	0.857	11.407
180	20.699	0.719	13.082
220	21.907	0.554	14.726
260	22.741	0.428	15.987
300	23.309	0.337	16.971

This sample shows two peaks (Fig-2b) for the C_{sh} vs T curve at 15K and 115K with values 0.4368R and 0.9564R . The peak at 15K arises due to two level system [$\mu=\pm(5/2)$ and $\mu=\pm(3/2)$] like that of $Er(OH)_3$. [5,9]

The nuclear spin of ^{167}Er in ground state is $I_g=7/2$ followed by first excited state $I_e=9/2$ at energy gap of 79.32 KeV. With the help of g-values the hyperfine constants (A and B) were found out to be 71.99×10^{-4} cm^{-1} and 310.5×10^{-4} cm^{-1} respectively. The value of EFG for 4f-electronic part was calculated using the CF energy levels and wavefunctions (Table-1) and was found to be nearly constant at and below 5mK . Using the temperature dependent and temperature independent part of EFG the value of EQP for ground (P_g) and first excited state (P_e) were computed .

Using the values of A, B and P the hyperfine levels were calculated. Due to hyperfine interaction I_g (=7/2) with electronic spin (S=1/2) splits into 7 doublets and 2 singlets with total width ~ 0.1242 cm^{-1} (Fig-3) . The first excited state I_e (=9/2) splits into 9 doublets and 2 singlets with total width~ 0.1550 cm^{-1} . The hyperfine specific heat was calculated in millikelvin temperature range .

For this sample two peaks was observed at 1.2 mK and 54.5 mK with magnitude 0.765R and 0.567R respectively [Fig-4a,4b]. It also varies as $1/T^2$ (where T represents absolute temperature) over a large temperature range (between 250 mK and 1K) with almost constant value $(C_{sh}/R)\times T^2 = 5427\ mK^2$ [Fig-4c] . Since the hyperfine specific heat value is comparatively high (0.8R) and measurable hence this property can be used in milikelvin thermometry . Measurements of specific heat of other RE-chlorides are welcome for comparison with these results.

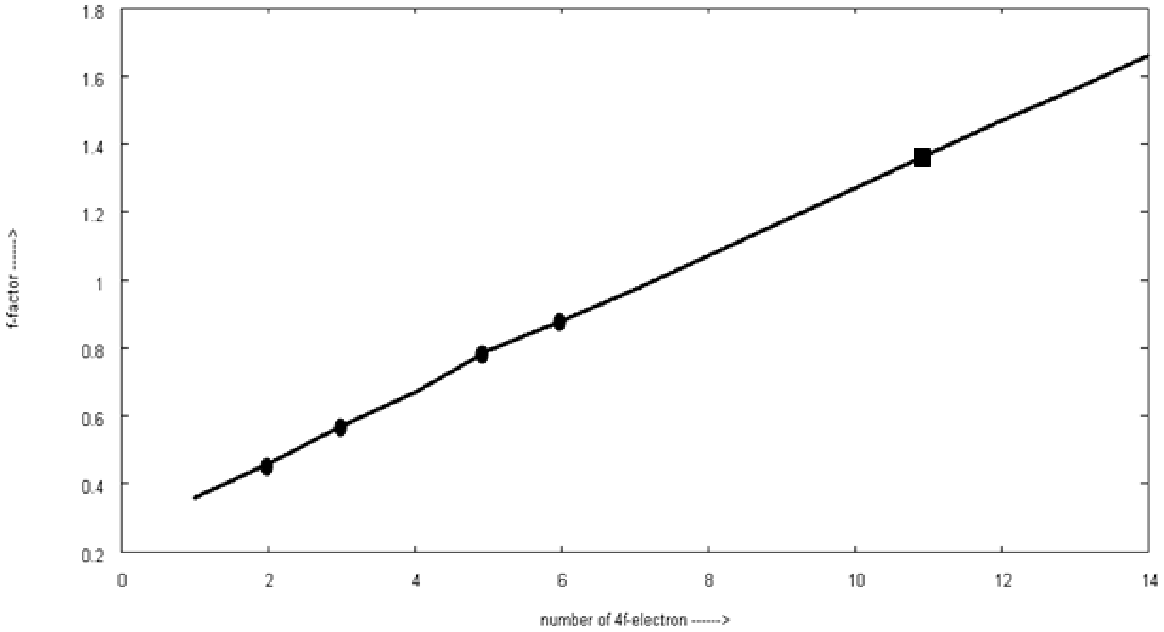

Fig -1 (f-factor vs number of 4f-electron of RE ions)

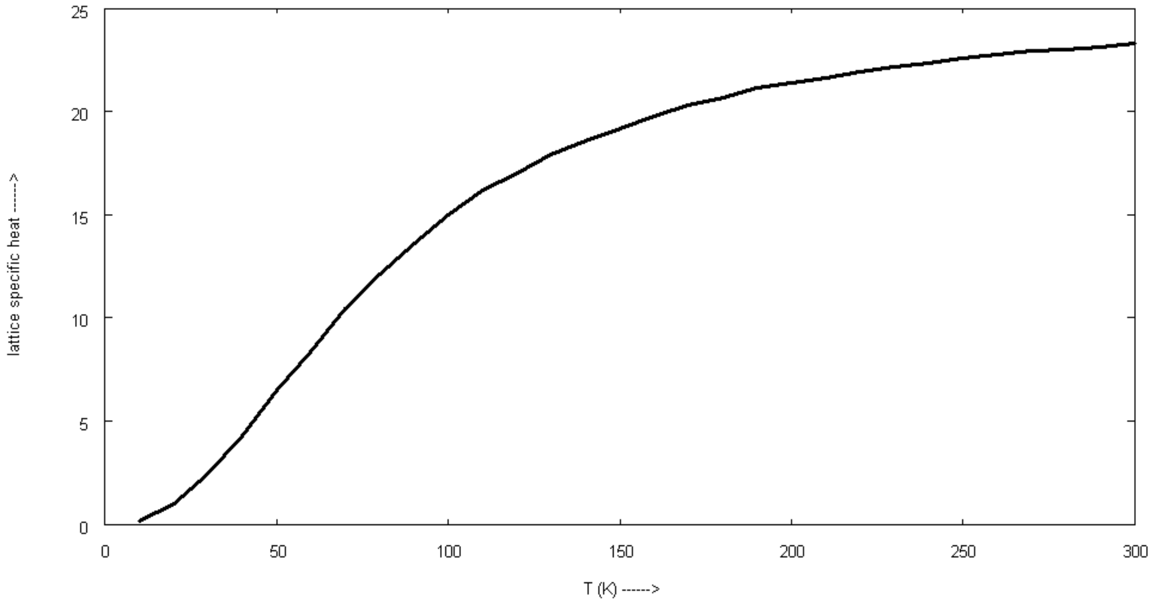

Fig2(a) Thermal variation of Lattice specific heat

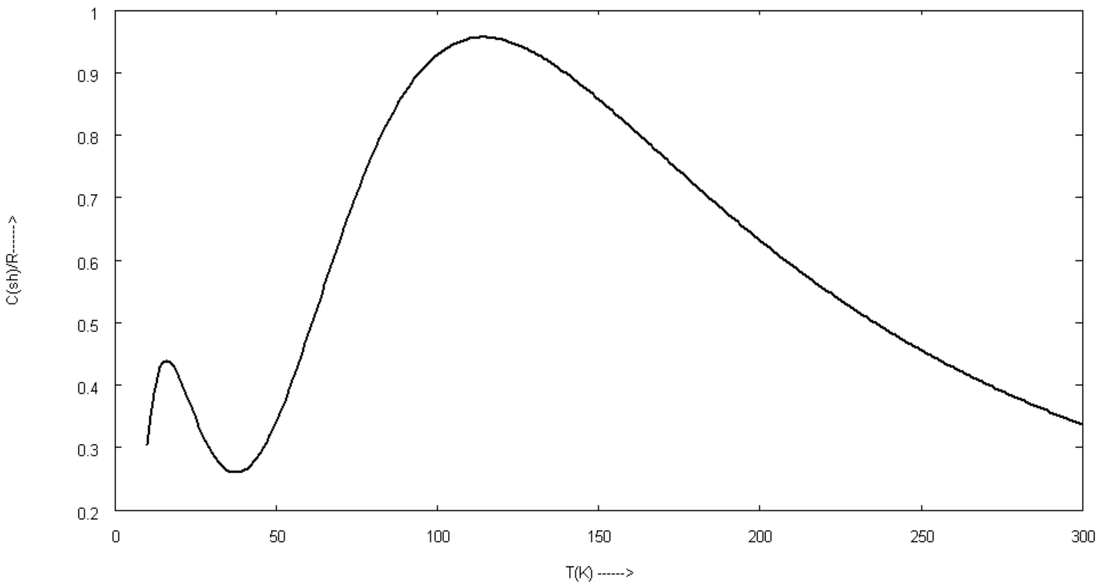

Fig2(b) Thermal variation of Schottky specific heat

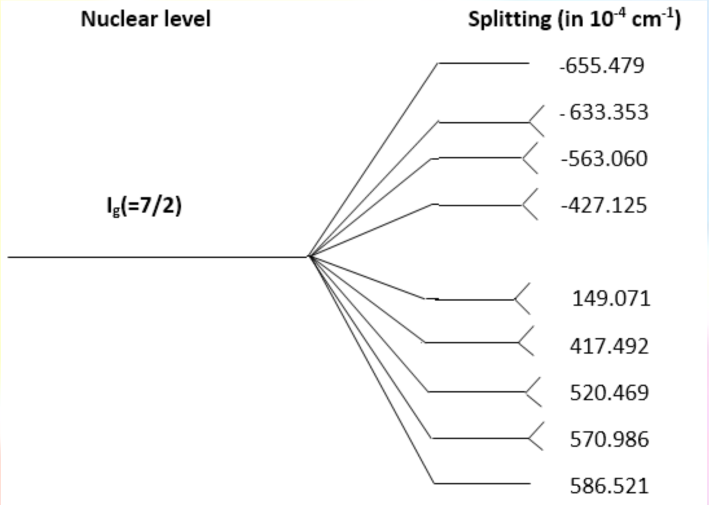

Fig 3 Hyperfine energy levels (not in scale)

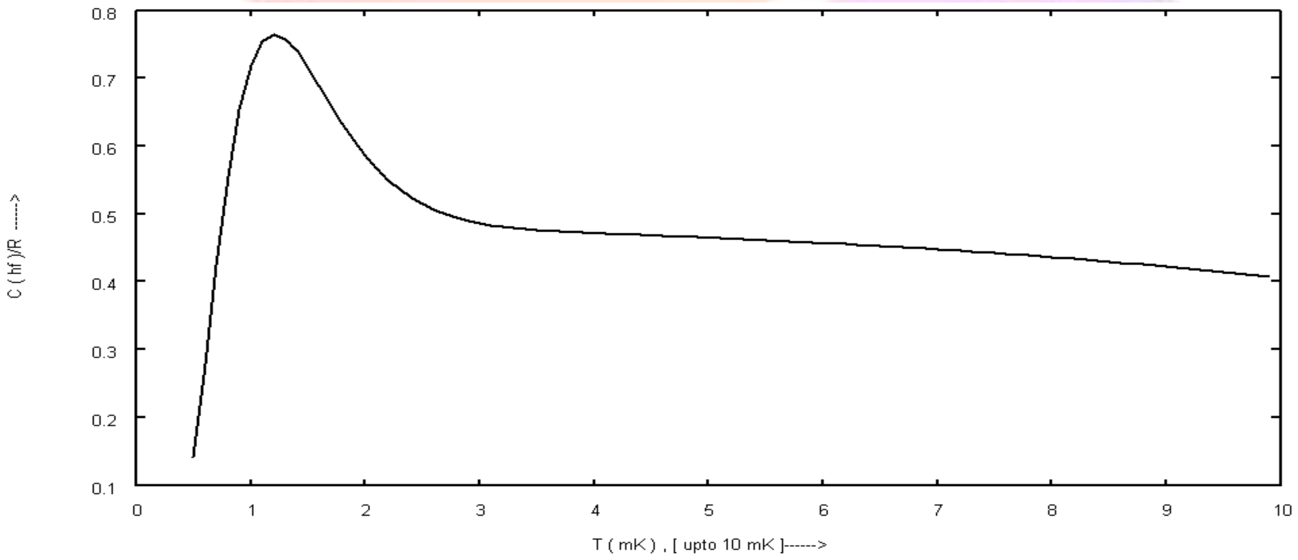

Fig-4a Thermal variation of Hyperfine specific heat (below 10mK)

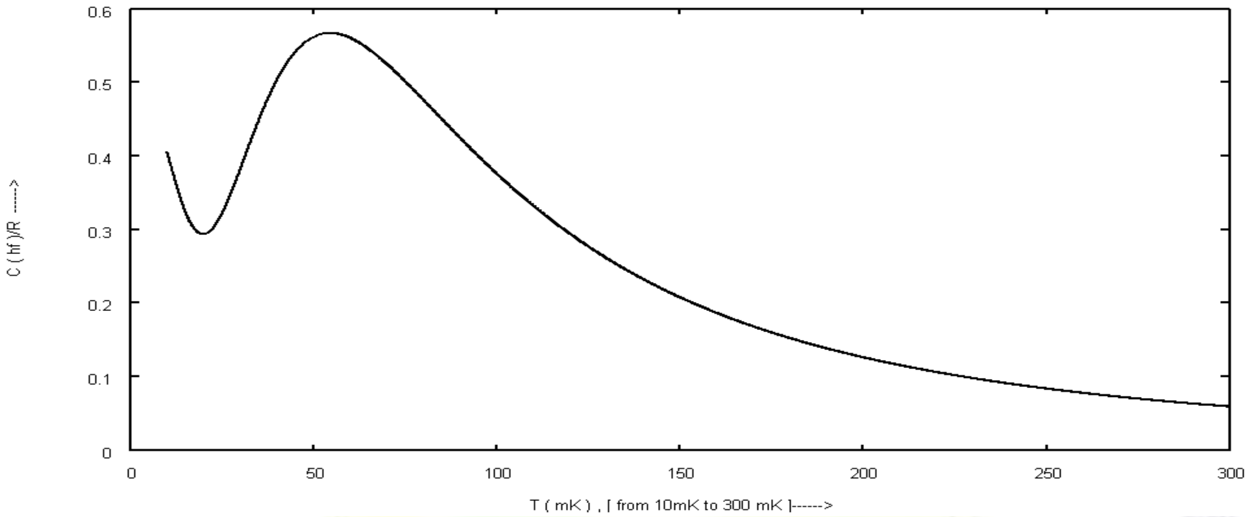

Fig-4b Thermal variation of Hyperfine specific heat (from 10mK – 300mK)

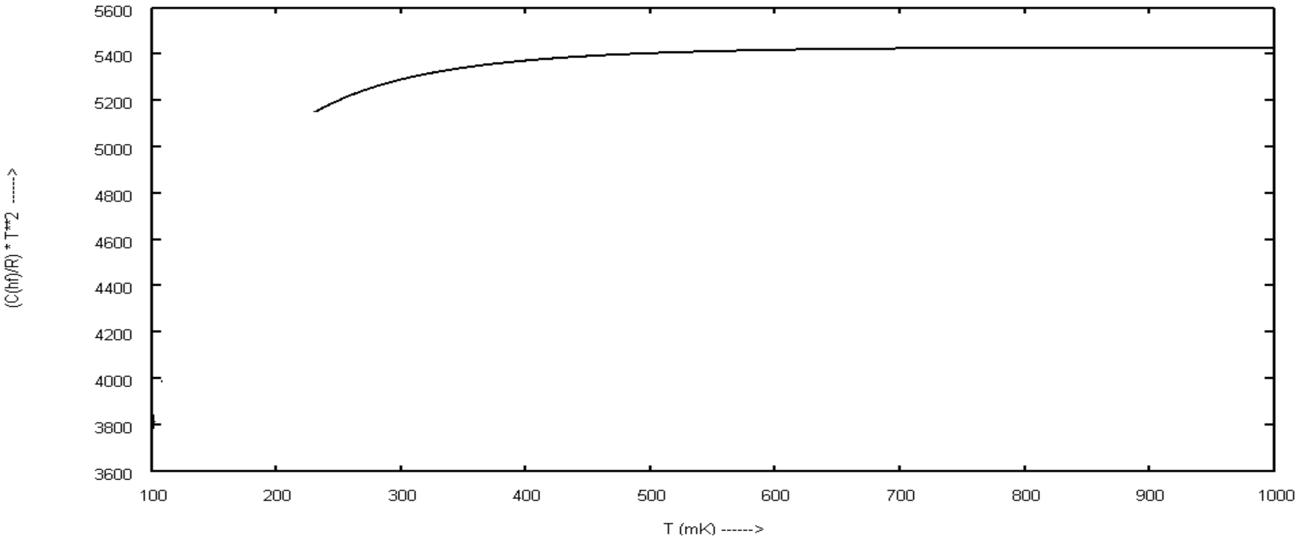

Fig-4c Thermal variation of $C_{hf}/R\times T^2$ (in mK^2)

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