

Physical properties of $R\text{Ir}_3$ ($R = \text{Gd}, \text{Tb}, \text{Ho}$) compounds with coexisting polymorphic phases

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Heat Capacity:

The total heat capacity of a material in the paramagnetic region consists of two contributions: electronic (γT) and Phononic (C_{phonon}). The phononic contribution was first explained by Einstein, who assumed that a solid composed of N atoms can be represented as $3N$ independent harmonic oscillators having same frequency [1, 2]. The Einstein contribution can be written as [1, 3],

$$C_E = \sum_N 3N_E R \frac{x^2 e^x}{[e^x - 1]^2}$$

where N_E is the number of Einstein oscillators, $x = \theta_E/T$, θ_E is the Einstein temperature. However, it was found that the Einstein model appears to be quite inadequate to describe the experimentally observed specific heat behavior at low temperature region for most of the solids [1, 2, 4]. Following this, Debye had modified Einstein model by assuming that the solid consisting of a set of coupled oscillator instead of independent oscillators [1, 2, 4], where the phononic contribution to heat capacity takes the following form [1, 3],

$$C_D = 9NR \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{[e^x - 1]^2}$$

where N_D is the number of Debye oscillators and $x = \theta_D/T$, θ_D being the Debye temperature. The modification proposed by Debye indeed able to explain the low temperature heat capacity data in much better way than Einstein model. The Debye model still cannot describe the experimental heat capacity behavior over the entire temperature region, as it works well below $\theta_D/50$ and above $\theta_D/10$ only [1]. The quantitative mismatch in the intermediate temperature region has its origin in the fact that the phonon dispersion phenomenon was not taken into account in the Debye model. Since neither a single Einstein model nor a single Debye model can describe the experimental outcome over the whole temperature range, a combination of both the contributions generally used to describe the overall heat capacity behavior [5, 6, 7, 8, 9, 10, 3], that can be expressed as [9, 1]

$$C_P = \gamma T + \sum_i \eta_i C_{E_i}(T) + \left(1 - \sum_i \eta_i\right) C_{E_i}(T) \quad \dots\dots\dots S1$$

The parameter η determines the relative weight age of the two contributions.

Critical behavior of the magnetization and susceptibility:

Critical analysis study utilizes the fact that any phenomena that take place in the vicinity of the phase transition

temperature can be associated with a power law behavior of the reduced temperature ($\varepsilon = \frac{(T - T_C)}{T_C}$). For example, magnetic correlation length ξ can be expressed as $\xi = \xi_0 |\varepsilon|^{-\nu}$, where ν is known as critical exponent.

Following the same argument, one can express several other physical quantities viz., $M_S(T)$, $\chi_0(T)$, $M(H, T = T_C)$, $C(T)$, etc. with similar power law expression as [11, 12, 13, 14]:

$$M_S(0,T) = M_0(-\varepsilon)^\beta \quad \varepsilon < 0, \quad \dots\dots S2$$

$$\chi_0^{-1} = \left(\frac{h_0}{M_0}\right)(\varepsilon)^\gamma \quad \varepsilon > 0, \quad \dots\dots S3$$

$$M(H,T_C) = A_0(H)^\frac{1}{\delta} \quad \varepsilon = 0, \quad \dots\dots S4$$

$$C(T) = C_0\varepsilon^{-\alpha} \quad \dots\dots\dots S5$$

where M_0 , h_0/M_0 , A_0 and C_0 are the critical amplitudes, M_S is the spontaneous magnetization, χ_0 is the initial susceptibility. Depending on the characteristic of various universality classes, viz. 2D Ising model, 3D Ising model, mean field, 3D Heisenberg model, tricritical mean field, XY model etc. the critical exponents α , β , γ and δ can assume different set of values (see table S1). Conversely by carrying out critical analysis and obtaining the values of α , β , γ and δ , one may associate the compound with the universality class it belongs to. The values of critical exponents associated with different universal class are given in table S1.

Table S1: Value of critical exponents according to different ideal model [15, 16, 17, 18].

	α	β	γ	δ
Mean field	0	0.5	1.0	3.0
2D Ising	0	0.12	1.75	15
3D Ising	0.11	0.32	1.24	4.82
3D Heisenberg	-0.11	0.36	1.38	4.90
3D XY	-0.007	0.34	1.34	4.8
Tricritical mean field	0.5	0.25	1.0	5.0

It must be pointed out here that although, the power law behavior expressed in eqns. S2, S3, S4, S5 are independent to each other, but the critical exponents are not so. The critical exponents can be linked using different scaling relations. For example, magnetization $M(H, T)$ can be expressed using two independent functions of H and T as,

$$M(H,T) = F(T) \times G(T,H) \quad \dots\dots\dots S6$$

where $F(T)$ is a function of T alone, while $G(T,H)$ is a function of both T and H . Solving analytically one can rewrite eqn. S6 as,

$$M(H,\varepsilon) = (\varepsilon)^\beta f_{\pm} \left[\frac{H}{\varepsilon^{\gamma+\beta}} \right] \quad \dots\dots S7$$

where f_+ and f_- are the functions of temperatures above and below T_C , respectively [11, 12]. Using different boundary conditions, one can obtain a scaling relationship,

$$\delta = 1 + \left(\frac{\gamma}{\beta} \right) \quad \dots\dots S8$$

which is widely known as Widom scaling relation [13, 19].

If the scaled or renormalized magnetization and magnetic field are defined as, $m = |\varepsilon|^{-\beta} M(H,\varepsilon)$ and $h = |\varepsilon|^{-(\gamma+\beta)} H$ eqn. S7 reduces to a simple form,

$$m = f_{\pm}(h) \quad \dots\dots S9$$

This equation is quite significant as it shows that with appropriate choice of a particular set of β , γ and δ the scaled magnetization m as a function of scaled field h taken at different temperatures can essentially be converged to two different universal curves: $f_+(h)$ for temperatures above T_C and $f_-(h)$ for temperatures below T_C .

As shown in eqns. S2, S3, S4, S5 different measurements can be employed to estimate different critical exponents. For example, by studying the isothermal magnetization close to critical temperature, eqn. S4 indicates that one can obtain information on δ (and subsequently on α and β). From table 1 we see that for mean field like variation δ is close to 3, that is eqn. S4 reduces to

$$M = A_0 H^{1/3} \quad \dots\dots S10$$

where A_0 is a constant. This is generally known as Arrott equation [20]. Using this equation a set of magnetic isotherms obtained experimentally near T_C can be turned into another set of parallel straight lines in the M^2 vs. H/M representation. This reconstructed magnetic isotherms are called Arrott plot [20]. The magnetic isotherm of Arrott plot that passes through origin defines the T_C . However, the material that does not obey mean field approximation cannot produce such set of parallel straight lines. A more generalized equation has been provided by Arrott and Noaks as [21],

$$(H/M)^{1/\gamma} = a \left(\frac{T - T_C}{T_C} \right) + b M^{1/\beta} \quad \dots\dots S11$$

(where a and b are constants) which is used to obtain a set of parallel straight lines in the $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ representation. This plot obeying Arrott-Noakes equation of state is often referred as modified Arrott plot [21]. Thus self consistent values of β , γ and δ can be obtained by same set of data (isothermal magnetization) using different analytical approach as presented in eqns. S2, S3, S4, S5 and S11.

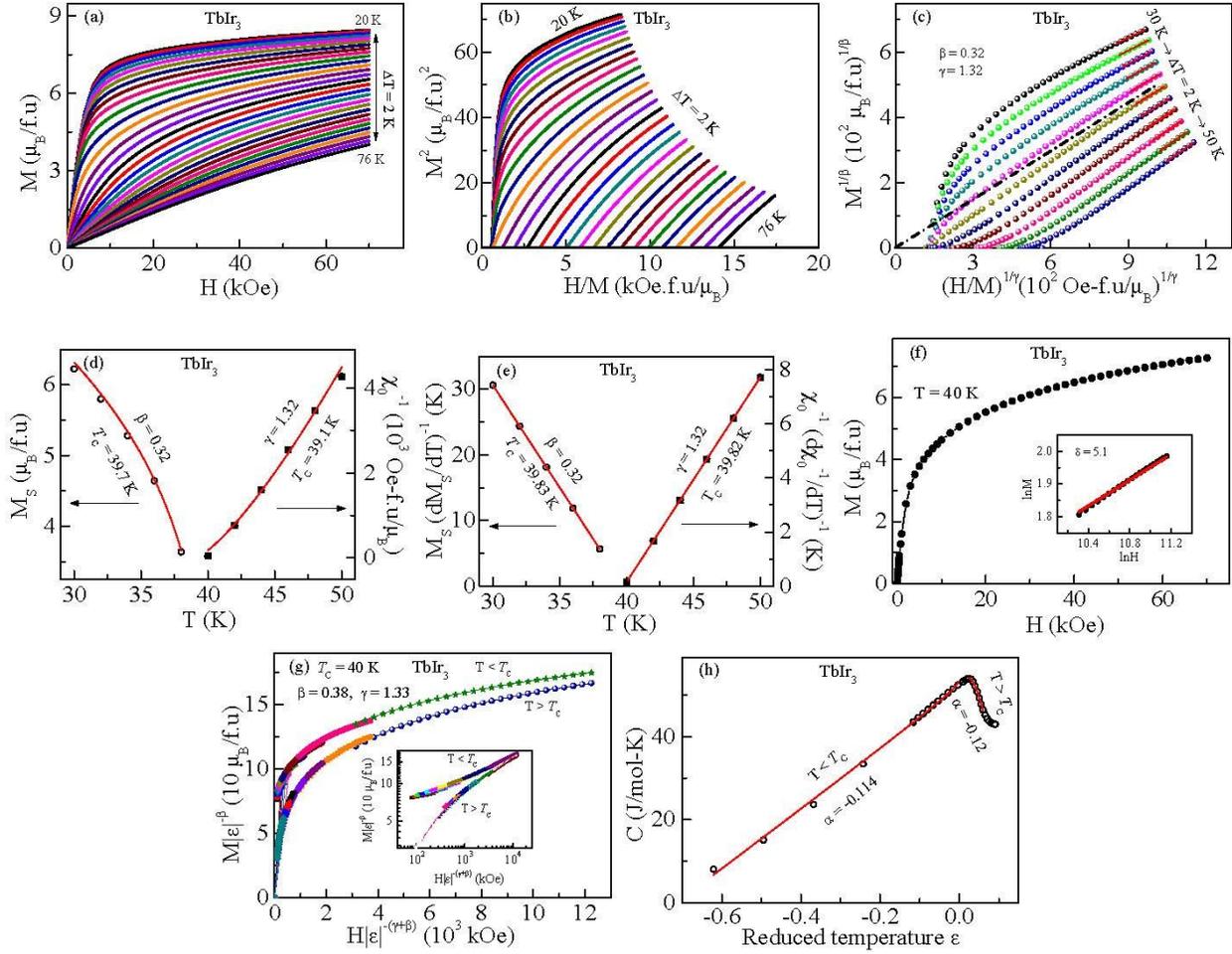


Figure S1: Critical behavior of TbIr₃: (a) Isothermal magnetization curves at temperatures around (T_C); (b) Arrott plot at different temperatures close to the Curie temperature (T_C); (c) Modified Arrott plot. Solid lines are the linear fit of the isotherms at high temperature region. The isotherm close to the Curie temperature ($T_C \sim 40$ K) almost passes through the origin; (d) Temperature dependence of spontaneous magnetization and inverse initial susceptibility. The solid lines are the fit to the power law eqns. S2, S3; (e) Kouvel-Fisher plot of spontaneous magnetization and inverse initial susceptibility. Solid lines are the linear fit to the data; (f) Critical isotherm close to the Curie temperature (T_C). The inset shows the same on log-log scale. The solid line is the linear fit following eqn. S4; (g) Scaled magnetization below and above T_C . This plot shows that all the data collapse onto two different curves: one below T_C and another above T_C . Inset shows the same on a log scale; (h) Heat capacity data on a reduced temperature scale below and above T_C . The solid line is the linear fit following eqn. (7).

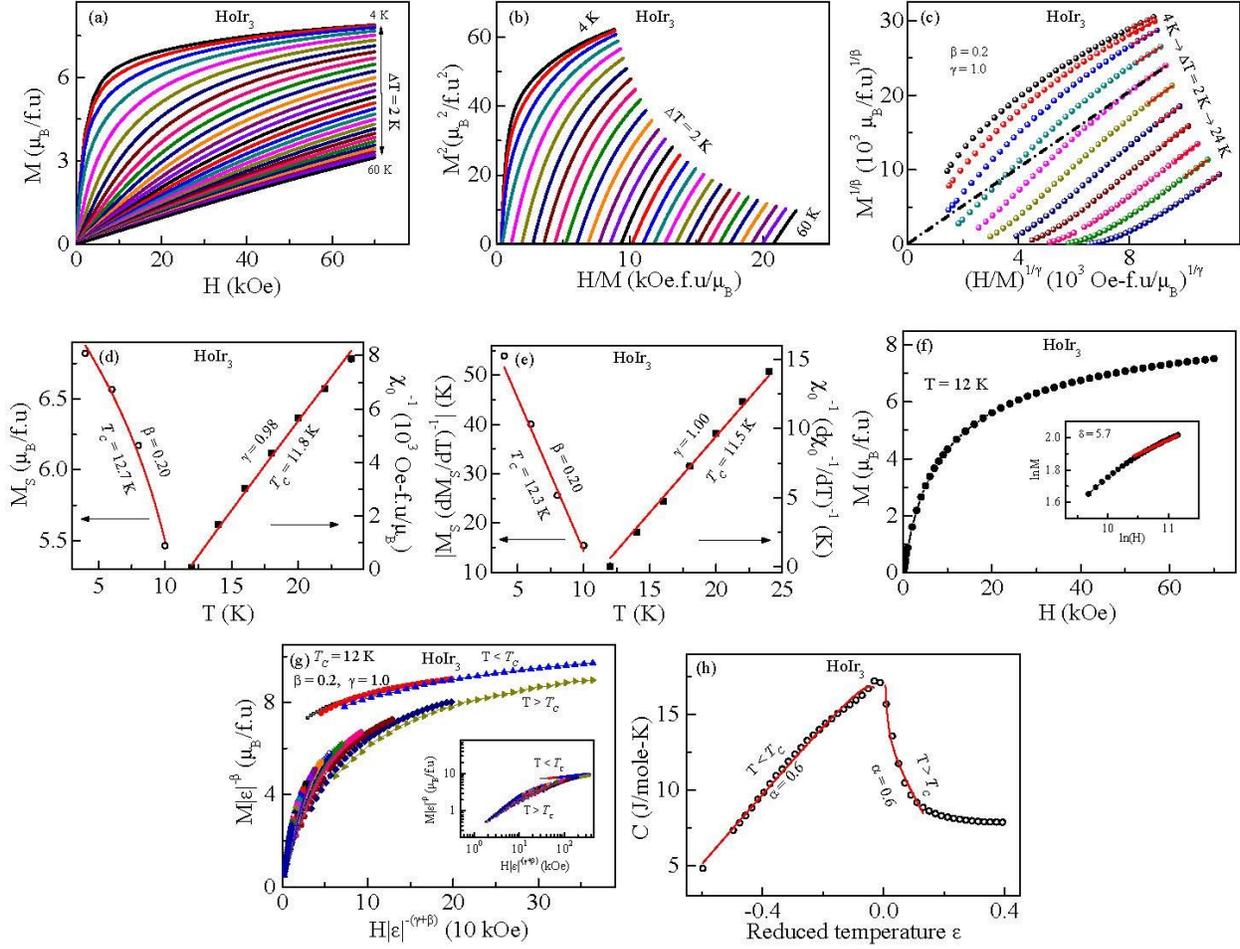


Figure S2: Critical behavior of HoIr_3 : (a) Isothermal magnetization curves at temperatures around (T_C); (b) Arrott plot at different temperatures close to the Curie temperature (T_C); (c) Modified Arrott plot. Solid lines are the linear fit of the isotherms at high temperature region. The isotherm close to the Curie temperature ($T_C \sim 12$ K) almost passes through the origin; (d) Temperature dependence of spontaneous magnetization and inverse initial susceptibility. The solid lines are the fit to the power law eqns. S2, S3; (e) Kouvel-Fisher plot of spontaneous magnetization and inverse initial susceptibility. Solid lines are the linear fit to the data; (f) Critical isotherm close to the Curie temperature (T_C). The inset shows the same on log-log scale. The solid line is the linear fit following eqn. S4; (g) Scaled magnetization below and above T_C . This plot shows that all the data collapse onto two different curves: one below T_C and another above T_C . Inset shows the same on a log scale; (h) Heat capacity data on a reduced temperature scale below and above T_C . The solid line is the linear fit following eqn. (7).

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