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Magnetic behaviour of yttrium-iron-transition metal mixed oxides

H B Lal, A N Thakur, K Gaur, M A Khan and V P Srivastava
Department of Physics, University of Gorakhpur, Gorakhpur-273 009, India

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Abstract : The compounds of yttrium-iron-transition metal mixed oxides of the type $YFeTO_4$ have been prepared by solid state reaction technique and characterised by XRD pattern The molar magnetic susceptibility (χ_M) of the powdered samples have been reported in the temperature range 300 to 1100 K All studied materials show a typical ferrimagnetic behaviour and χ_M^{-1} *vs* T plot can be expressed in terms of standard relations for ferri-magnetic material The slope of asymptotic line to the curve, yields an average magneton number which indicates that all materials are perfectly ionic The molecular field parameters α, β and γ have been evaluated using Neels two sublattice model (NTSM). Both α and β have been found negative indicating angular arrangement of magnetic ions in the magnetic ground state of the studied materials.

Keywords : Magnetic susceptibility, transition metal oxides, sublattice

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1. Introduction

Rare-earth and transition elements have unfilled $4f$ and $3d$ orbitals. Due to this reason, they yield variety of materials with interesting and useful magnetic properties. These have not only enriched our understanding but have found numerous applications [1–3]. We have prepared a series of rare-earth-transition metal compounds with general formula $R_ETT'O_4$ where R_E stands for rare-earth and T and T′ for transition metals. We have already reported the electrical transport studies of $YFeTO_4$ where T = Fe, Cr, Mn, Co and Ni [4] and magnetic behaviour of $GdFeTO_4$ [5]. This paper reports results of our study on the magnetic behaviour of compounds with general formula $YFeTO_4$ with T = Fe, Cr, Mn, Co and Ni. So far, no study of this kind has been reported on these compounds. Only some studies have been reported on YFe_2O_4 which are related with low temperature phase transition [6,7], neutron diffraction [8,9], Mossbaur studies [10,11] and dielectric properties [12].

2. Material preparation and characterization

The series of compounds with general formula $YFeTO_4$ have been prepared with the basic materials Y_2O_3, Fe_2O_3 and oxides Cr_2O_3, NiO, CoO and MnO_2. These materials were procured from standard forms and have stated purity of 99.9 percent to 99.99 percent. The stoichiometric amount of these oxides were mixed and heated in a silica crucible for 50 hrs at a temperature of about 1400 K. In this process, the mixture was subjected to one intermediate grinding and the final product was cooled down at a slow rate. The prepared compounds undergo following solid state reactions :

$$2Y_2O_3 + 4Fe_2O_3 \xrightarrow[\text{Air}]{1400\ \text{K}} 4YFe_2O_4 + O_2,$$

$$2Y_2O_3 + 2Fe_2O_3 + 2Cr_2O_3 \xrightarrow[\text{Air}]{1400\ \text{K}} 4YFeCrO_4 + O_2,$$

$$Y_2O_3 + Fe_2O_3 + 2MnO_2 \xrightarrow[\text{Air}]{1400\ \text{K}} 2YFeMnO_4 + O_2,$$

$$Y_2O_3 + Fe_2O_3 + 2CoO \xrightarrow[\text{Air}]{1400\ \text{K}} 2YFeCoO_4,$$

$$Y_2O_3 + Fe_2O_3 + 2NiO \xrightarrow[\text{Air}]{1400\ \text{K}} 2YFeNiO_4.$$

The weight loss corresponding to loss of oxygen on the right hand side of the above reaction was observed in all cases except in $YFeMnO_4$. In this case, loss was about 4.0 percent against expected 5.3 percent. Other details of preparation are described elsewhere [13].

To confirm the complete formation of the prepared compounds, XRD pattern were obtained for each material using CuK_α radiation with $\lambda = 0.15418$ nm. From XRD pattern the values of interplaner spacing d_{hkl} have been obtained using relation

$$d_{hkl} = \frac{0.15418}{2\sin\theta}(\text{nm}) \tag{1}$$

From d_{hkl} values, structure of the prepared compounds have been resolved using standard procedure [13]. All the peaks have been identified and assigned proper hkl values and lattice parameters have been evaluated. It has been found that all studied materials have orthorhombic unit cell with lattice parameters a_0, b_0 and c_0. Using these values d_{hkl} have been calculated from the ralation,

$$d_{hkl} = b_0 / \left[(h/a)^2 + k^2 + (1/c)^2\right]^{1/2}, \tag{2}$$

where $a = a_0/b_0$, $c = c_0/b_0$. We tried to assign the indexes 200, 020, 400, 040 and 004 to appropriate peaks by trial method and then the possible values of a_0, b_0 and c_0 are calculated using eq. (2). With these values of a_0, b_0 and c_0, the theoretical values for different d_{hkl} have been evaluated. The experimental values of d_{hkl}, relative intensity of

peak (I/I_0), assigned hkl values and calculated d_{hkl} values using assigned index are given in Table 1.

Table 1. d_{hkl} (expt.) values corresponding to peak observed in XRD, their relative intensity (I/I_0), calculated values of d_{hkl} and assigned h, k, l values.

d_{hkl} (expt.)	$I/I_0 \times 100$	d_{hkl} (Theo.)	[h, k, l]
	(a) YFe_2O_4		
0.4375	12	0.4375	[0 0 2]
0.3708	21	0.3708	[0 2 0]
0.3069	100	0 3069	[2 0 0]
0.2706	70	0.2698	[2 1 1]
0.2660	25	0 2634	[1 0 3]
0 2522	47	0.2513	[2 0 2]
0.2212	15	0.2188	[0 0 4]
0.2080	10	0 2080	[2 2 2]
0.2036	10	0.2031	[1 3 2]
0.1877	40	0 1880	[2 3 1]
0 1845	25	0 1854	[0 4 0]
0 1701	29	0 1703	[0 1 5]
0 1603	31	0 1606	[2 2 4]
0.1488	20	0.1492	[2 4 2]
0.1457	17	0 1458	[0 0 6]
	(b) $YEeCrO_4$		
0 4332	12	0.4332	[0 0 2]
0 3641	10	0 3640	[0 2 0]
0.3069	100	0 3069	[2 0 0]
0.2698	21	0 2688	[2 1 1]
0.2660	28	0.2685	[0 1 3]
0 2518	14	0.2504	[2 0 2]
0.2080	11	0 2063	[2 2 2]
0.1877	47	0 1861	[0 2 4]
0.1675	13	0 1678	[0 4 2]
0 1600	33	0 1592	[2 2 4]
	(c) $YFeMnO_4$		
0.4353	11	0.4353	[0 0 2]
0.3693	11	0 3693	[0 2 0]
0 3121	37	0 3164	[1 2 0]
0 3069	100	0.3069	[2 0 0]
0 2702	38	0 2701	[0 1 3]
0.2652	26	0 2624	[1 0 3]
0.2522	28	0.2508	[2 0 2]
0.2206	11	0 2177	[0 0 4]
0.2080	12	0.2075	[2 2 2]
0 1877	47	0.1877	[0 3 3]
0.1845	16	0.1846	[0 4 0]
0.1602	34	0 1601	[2 2 4]
0.1488	13	0 1487	[2 4 2]

Table 1. *(Cont'd).*

d_{hkl} (expt.)	$I/I_0 \times 100$	d_{hkl} (Theo.)	[h, k, l]
	(d) $YFeCoO_4$		
0.4210	11	0 4210	[0 0 2]
0.3708	11	0.3708	[0 2 0]
0.3079	100	0.3079	[2 0 0]
0.2714	40	0.2782	[0 2 2]
0.2663	28	0.2694	[2 1 1]
0.2529	31	0.2554	[1 0 3]
0.2449	30	0 2485	[2 0 2]
0.2085	11	0.2065	[2 2 2]
0.2034	10	0.2014	[1 3 2]
0.1881	49	0.1879	[2 3 1]
0 1848	18	0 1854	[0 4 0]
0.1603	35	0 1588	[2 2 4]
0 1560	12	0.1551	[1 3 4]
0 1490	13	0.1486	[2 4 2]
	(e) $YFeNiO_4$		
0 4353	12	0 4353	[0 0 2]
0.3079	100	0.3079	[2 0 0]
0 2714	26	0.2701	[0 1 3]
0.2667	24	0.2625	[1 0 3]
0 2529	18	0.2514	[2 0 2]
0 2094	35	0.2078	[2 2 2]
0 1877	39	0 1877	[0 3 3]
0.1698	10	0.1700	[0 4 2]
0 1603	26	0 1602	[2 2 4]
0.1480	15	0.1485	[4 1 1]

All the observed peaks in XRD, have been identified and assigned proper h, k, l values. The agreement between d_{hkl} (expt.) and d_{hkl} (theo.) is very good. All materials have been found to have orthorhombic unit cell with unit cell parameter a_0, b_0 and c_0 as given in Table 2.

Table 2. Structural parameters of prepared $YFeTO_4$ compounds

Compounds	Lattice parameters (nm)			Unit cell volume	Calculated density
	a_0	b_0	c_0	$m^3 \times 10^{28}$	Kg $m^{-3} \times 10$
YFe_2O_4	0.6138	0.7416	0.8750	− 3.982	4 41
$YFeCrO_4$	0.6138	0.7280	0.8664	3.872	4 48
$YFeMnO_4$	0.6138	0.7386	0 8706	3.947	4 44
$YFeCoO_4$	0.6158	0.7416	0.8420	3.845	4 63
$YFeNiO_4$	0.6158	0.7386	0.8706	3.960	4 49

3. Measurement of magnetic susceptibility

Magnetic susceptibility measurement has been done using Faraday method. In this method, one requires only 50–100 mg of the sample as well as standard material. The setup have been assembled and consists of a magnetic balance (of 10^{-5} gm accuracy with all control external, from Keroy, India), a tapered pole pieces (2" diameter from 4" base at angle of 30°) electromagnet and constant current power supply (both from Pollytronic, India). The pole gap is variable but has been fixed at a separation of 4.8 cm. At this pole gap, the magnetic field in constant $H\left(\frac{dH}{dz}\right)$ region, which lies about 2.5 cm above the centre of the pole, is about 1.5×10^5 Am^{-1} at 2A current in the electromagnet coil. A pyrex tube of 2 cm long and 0.5 cm dia has been used as a sample holder. $Gd_2(WO_4)_3$ with molar magnetic susceptibility value 6.85×10^{-7} at 300 K has been used as standard substance.

The standard material and the sample is hanged from the hook provided in the pan of the balance in constant $H\left(\frac{dH}{dz}\right)$ region in the pyrex tube and weight is measured in both cases, with and without applied magnetic field. The molar magnetic susceptibility of the sample have been obtained from the relation

$$\chi_M = \left(\frac{\Delta m}{\Delta m_s}\right)\left(\frac{m_s}{m}\right)\chi_S,$$

Δm and Δm_s are changes in the weights of the sample and standard substance, m and m_s are their masses and χ_S the molar magnetic susceptibility of the standard substance. Being a relative method most of the error are automatically eliminated except the error in the measurement of mass m and weight change Δm. The maximum probable error in these measurements, has been about 2% at lower temperature ($T < 500$ K). But it increases with the increase of temperature, because hot air movement disturbs the sample holder inspite of closed one end of the furnace, and becomes as high as 5% around 1000 K [13,14].

4. Result and discussion

The molar magnetic susceptibility (χ_M) of all the compounds have been measured in both heating and cooling cycles. No hysteresis was observed in χ_M and values were found same in both heating and cooling cycles. However, a small weight loss have been noticed in heating cycle probably due to presence of moisture. The results are presented in Figure 1 as χ_M^{-1} *vs* T plot. It is seen from the figure that the nature of all the plots is essentially similar. In general, χ_M^{-1} *vs* T plots are linear at higher side of temperature, however, there is systematic trend of experimental points towards temperature axis at lower side of temperature. The curves are thus similar to a standard ferrimagnetic material and systematic downward trend is due to onset of short range magnetic interaction at lower side of temperature. We have tried to fit the experimental

points to the standard equation of ferrimagnetism [15] given below by choosing suitable parameters

$$\frac{1}{\chi_M} = \frac{T-\theta_a}{\bar{C}_M} \qquad \frac{\theta_b^2}{\bar{C}_M(T-\theta)} \tag{3}$$

where χ_M is the molar magnetic susceptibility, $\bar{C}_M$ is the average value of Curie-constant, θ_a is the asymptotic Curie temperature and θ_b and θ are parametric temperatures

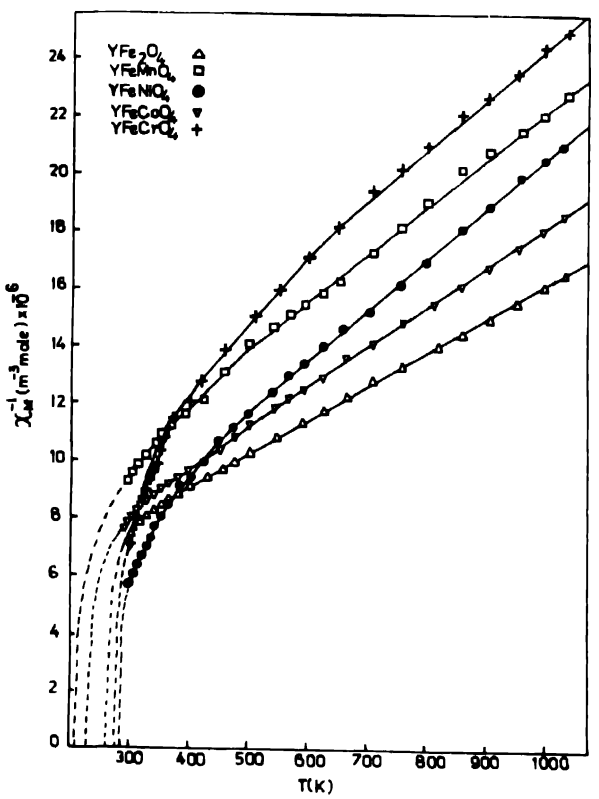

Figure 1. Plots of the inverse of molar magnetic susceptibility (χ_M^{-1}) against absolute temperature (T) for the studied materials

The curves using eq. (3) are drawn by full line in respective χ_M^{-1} *vs* T plots. It is seen that experimental χ_M points can be well fitted by eq. (3) over wide temperature range. The values of $\bar{C}_M$, θ_a, θ_b and θ are given in Table 3.

The ferrimagnetic Curie (or Neel) temperature have been evaluated using condition $T \to T_c$, $\chi_M^{-1} \to 0$. This gives

$$(T_c - \theta_a)(T_c - \theta) = \theta_b^2. \tag{4}$$

The real and positive values of T_c are meaningful and have been evaluated using eq. (4) These values are also given in Table 3. The compound $YFeTO_4$, if taken as ionic, will

contain three types of magnetic ions namely Y^{3+}, Fe^{3+} or Fe^{2+} and T^{3+} or T^{2+}. Out of these, Y^{3+} is non-magnetic and hence they have only two types of magnetic ions namely Fe^{3+}

Table 3. Magnetic parameters for full line curves for the studied compounds

Compounds	θ_a (K)	θ (K)	θ_b (K)	T_c (K)	$\bar{C}_M$ $(mol^{-1}\ m^3K) \times 10^5$
YFe_2O_4	−465	238	69	245	9 17
$YFeCrO_4$	−485	213	178	255	6 04
$YFeMnO_4$	−505	240	69	246	7 45
$YFeCoO_4$	−365	240	64	242	7 50
$YFeNiO_4$	−360	210	162	253	6 60

(or Fe^{2+}) and T^{3+} (or T^{2+}). Therefore, the molar magnetic susceptibility (χ_M) of these compounds at temperatures much higher than T_c can be expressed by the relation

$$\chi_M = \frac{N\mu_B^2\mu_0}{3k}\left[\frac{p_1^2}{T-\theta_{a_1}} + \frac{p_2^2}{T-\theta_{a_2}}\right], \tag{5}$$

where N is Avogadro's number, μ_B is Bohr magneton, μ_0 is the permeability constant, k is Boltzman constant, p_1 and p_2 are the magneton numbers of two types of magnetic ions and θ_{a_1} and θ_{a_2} are paramagnetic Curie-temperatures which takes into account the effects of various interactions. Assuming $\theta_{a_1} \simeq \theta_{a_2}$, we can write the above equation as

$$\chi_M = \frac{N\mu_B^2\mu_0}{3k}\left[\frac{2\bar{p}^2}{T-\theta_{a_1}}\right]$$

and

$$\chi_M^{-1} = \frac{3k}{2N\mu_B^2\mu_0\bar{p}^2}(T-\theta_{a_1}), \tag{6}$$

where $\bar{p}^2 = \dfrac{p_1^2+p_2^2}{2}$ is the square of average effective magneton number per ion. The line represented by eq. (6) must be asymptotic to curve given by eq. (3). Comparing eq. (6) with the asymptotic equation of the curve given by eq. (3) one gets $\theta_a = \theta_{a_1}$ and

$$\bar{C}_M = \frac{2N\mu_B^2\mu_0^2\bar{p}^2}{3k} \tag{7}$$

or

$$\bar{p}^2 = \frac{3k\bar{C}_M}{2N\mu_B^2\mu_0}. \tag{8}$$

The experimental value of $\bar{p}$ can be calculated from the evaluated value of $\bar{C}_M$. The theoretical values of p_1 and p_2 are known. Hence, one can obtain the theoretical value of $\bar{p}$. The experimental and theoretical values of $\bar{p}$ are given in Table 3 together with the magnetic ions used to obtain the theoretical value of $\bar{p}$.

It is seen from Table 4 that there exists a good agreement between the theoretical and experimental values of $\bar{p}$. This indicates that all studied materials are essentially ionic and magnetic states of the ion are as indicated in the last column of Table 4. It can also be noticed that in $YFeCrO_4$ and $YFeMnO_4$ compounds, there exist Cr^{3+} and Mn^{3+} ions and they substitute Fe^{3+} ions. This is quite reasonable in view of the natural valency of these elements.

Table 4. Theoretical and experimental values of $\bar{p}$ together with the magnetic ions used to obtain theoretical value of $\bar{p}$

Compounds	Values of $\bar{p}$		Magnetic ions	
	Theo	Expt.		
YFe_2O_4	5.43	5.41	Fe^{3+}	
$YFeCrO_4$	4.42	4.39	Cr^{3+}	Fe^{2+}
$YFeMnO_4$	4.90	4.88	Mn^{3+}	Fe^{2+}
$YFeCoO_4$	5.00	4.90	Fe^{3+}	Co^{2+}
$YFeNiO_4$	4.64	4.59	Fe^{3+}	Ni^{2+}

Having fitted the data into the well known equation of ferri-magnetic material and recognising the magnetic ions it is natural to attempt to investigate the molecular field parameters and magnetic ground state of studied materials. For this, let us use Neel's two sub-lattice model (NTSM) of ferrimagnetism [15]. This is justified, because $YFeTO_4$ contains only two types of magnetic ions as given in Table 4. We shall adopt the following terminology for the molecular field constants (τ_{AA}, τ_{BB}, τ_{AB}) between the sublattices A and B as discussed by Goodenough [15].

$$\tau_{AA} = \alpha n,\ \tau_{BB} = \beta n \text{ and } \tau_{AB} = -n, \tag{9}$$

where α and β are dimensionless constants. Using above nomenclature θ_a, θ_b and θ can be expressed in terms of α, β, n and Curie constants for two sublattices namely C_A and C_B as

$$\theta_a = \frac{-n}{C}\left[2C_AC_B - \alpha C_A^2 - \beta C_B^2\right],$$

$$\theta_b = \frac{n}{C}\left[C_A(1+\alpha) - C_B(1+\beta)\right]\sqrt{C_AC_B}$$

$$= \frac{n}{C}(C_AC_B)(2+\alpha+\beta), \tag{12}$$

with $C = C_A + C_B$.

The values of θ_a, θ_b and θ are known from fitting the curve and are given in Table 3. $C = \overline{C}_M$ is also given in Table 3. The number of trivalent and divalent $3d$ metal ions are known for each compound. The theoretical value of magneton number of these ions is also known

and there number in each material is also equal. Thus, it is easy to evaluate C_A and C_B and also n. α and β using eqs. (9) to (12). The evaluated values of these parameters are given in Table 5.

Table 5. Molecular field parameters of $YFeTO_4$

Compounds	α	β	n (mole m^{-3})	C_A ($mole^{-1}\ m^3K$)	C_B ($mole^{-1}\ m^3K$)
YFe_2O_4	–0.254	–0.389	7.850×10^4	5.48×10^{-5}	3.75×10^{-5}
$YFeCrO_4$	–0.091	–0.711	1.224×10^5	3.75×10^{-5}	2.34×10^{-5}
$YFeMnO_4$	–0.171	–0.352	8.61×10^4	3.75×10^{-5}	3.75×10^{-5}
$YFeCoO_4$	–0.276	–0.016	8.05×10^4	5.48×10^{-5}	2.34×10^{-5}
$YFeNiO_4$	–0.189	–0.142	1.21×10^5	5.48×10^{-5}	1.25×10^{-5}

It is seen from Table 5 that α and β are negative but their magnitude is less than unity. This indicates that the interactions between the ions of two sublattices (nearest neighbour '*nn*' interaction) as well as between the ions of the same sublattices (next nearest neighbours '*nnn*' interactions) are antiferromagnetic. Negative values of α and β are not very common in NTSM (Neel's two sublattice model) and hence, it is interesting to discuss its implication on the validity of above model as well as in the ground state magnetic structure of the studied materials. As is well known that basic assumption of NTSM is strong antiferromagnetic *nn* interaction which are much stronger than *nnn* interactions. If *nnn* interactions are ferromagnetic in the above model, then all the magnetic interaction lead to a ground state in which localized magnetic moments are aligned either parallel or antiparallel to each other. Contrary to that if *nnn* interactions are antiferro-magnetic (α or $\beta < 0$) but if these interactions are much weaker compared to *nn* interactions then they will lead to a ground state in which magnetic moments are not aligned parallel or antiparallel to each other but have angular arrangement. With α, β negative and their magnitude less than unity, the latter situation leading to angular arrangement of magnetic moments in the ground state seems valid for the studied materials.

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