Magnetic Remanence in $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ (RE = Tb, Dy, Ho) Single Crystals

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Abstract

Single crystals of $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ ($x \sim 0.1, 0.4$; RE = Tb, Dy, Ho) have been prepared as a solid solution by Sn flux reactions of the elements. They crystallize in the $\text{Ca}_{14}\text{AlSb}_{11}$ structure type in the $I4_1/acd$ space group. The RE^{3+} preferentially substitutes on the Yb(1) site which is the smallest volume Yb containing polyhedron. In the case of Ho^{3+} , a small amount of Ho^{3+} also substitutes on the Yb(4) site. The ferromagnetic ordering temperature of $\text{Yb}_{14}\text{MnSb}_{11}$ is reduced from 53 K to 41 K as x increases and dependent on the identity of the RE. This is attributed to the reduction in carriers and reduced screening of the Mn^{2+} local moment. The effective moments, μ_{eff} , agree well with the calculated moments assuming the RE substitutes as a 3+ cation. The largest coercive field is observed for RE = Dy (1000 Oe). For the maximum x of $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ there are enough carriers for the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism of magnetic coupling *via* conduction electrons to still be valid in describing the ferromagnetic ordering.

Graphical Abstract

Keywords

Zintl phase; ferromagnetism; hysteresis; $\text{Yb}_{14}\text{MnSb}_{11}$; Kondo; half-metal

1. Introduction

$\text{Yb}_{14}\text{MnSb}_{11}$ has unique magnetic properties and has been described as an example of an underscreened Kondo system [1]. $\text{Yb}_{14}\text{MnSb}_{11}$ has a large, complex unit cell, consisting of 14 Yb^{2+} cations, a $[\text{MnSb}_4]^{9-}$ tetrahedron, a Sb_3^{7-} linear trimer, and 4 Sb^{3-} anions, with 8 formula units per unit cell (Figure 1) [2]. The magnetic properties of $\text{Yb}_{14}\text{MnSb}_{11}$ can be completely described as arising from the MnSb_4 tetrahedral unit, as the Yb atoms in this compound have been shown to be Yb^{2+} [3]. The Mn in MnSb_4 has been shown to be Mn^{2+} [4, 5]. The unpaired spins of the Mn^{2+} ferromagnetically order below 53 K [6]. Despite Mn^{2+} having 5 unpaired electrons, only 4 spins are observed in the magnetization data [2]. This has been attributed to a hole associated with Sb on the tetrahedra and its anti-parallel electron screening one of the Mn moments [4, 5]. The fact that only one of the 5 unpaired electrons is screened leads to the description of an underscreened Kondo system since in a normal Kondo system localized spins are fully screened. The ferromagnetic ordering is best described as arising from Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling, where the magnetic moments are coupled through the mobile charge carriers [2].

Figure 1: Unit cell of $\text{Yb}_{14}\text{MnSb}_{11}$ viewed down the b axis, showing the MnSb_4 tetrahedra and the linear Sb_3 units. Blue and orange spheres represent Sb and Mn, respectively. Green spheres indicate Yb(1), red spheres indicate Yb(2), yellow spheres indicate Yb(3), and purple spheres indicate Yb(4).

$\text{Yb}_{14}\text{MnSb}_{11}$ is also an excellent high temperature p-type thermoelectric material [7, 8]. Solid solutions of $\text{Yb}_{14}\text{MnSb}_{11}$ have been recently prepared in order to increase the thermoelectric figure of merit of this p-type high temperature material [7]. Solid solutions of La [9, 10], Ce [11], Tm [12, 13], and Lu [14] substitution for Yb, Al [15] and Zn [16] for Mn, and Ge [17] and Te [18] for Sb have been reported with an emphasis on controlling carrier concentration for thermoelectrics, but these new solid solutions are also of interest as new magnetic materials [11].

However, in many cases, the magnetization has not been reported since the emphasis of the research has been on thermoelectric properties. The introduction of rare earths with partially filled *f*-orbitals is expected to provide new magnetic ordering in this structure. In particular, in intermetallic compounds of rare earth elements, RE, and transition metals, it is possible to obtain exotic magnetic order of 4*f* and 3*d* electrons [19].

Studies of the magnetic properties have been published for Yb_{14-x}RE_xMnSb₁₁ (RE = La, Ce, and Tm). The maximum amount of each RE substituted for Yb was determined to be 0.7 for La, 0.6 for Ce, and 0.5 for Tm [10-12]. In the case of Ce, site preferences are apparent where Ce initially substitutes on the Yb(2) site and when $x \geq 0.3$, it also substitutes on Yb(4) [11]. These sites have the largest volume as indicated by Hirshfeld surface analysis of chemical bonding [20]. Low temperature magnetization vs field data of samples with Ce substitution indicate that the Ce³⁺ moment does not participate in the ferromagnetic ordering of the material [11]. Temperature dependent magnetization data for La³⁺, Tm³⁺, and Ce³⁺ substitutions show a decrease in the magnetic ordering temperature, which is attributed to the reduction in carrier concentration result in an increase in the effective magnetic moment of the material. This is due to the additional electron introduced by substituting a 3+ cation for a 2+ cation filling the hole associated with the MnSb₄ tetrahedron and thereby reducing the screening of the 3*d* electron. A further enhancement of the effective magnetic moment is observed for Tm³⁺ and Ce³⁺ substitutions due to the *f* moments introduced by these cations.

Tb³⁺, Dy³⁺, and Ho³⁺ possess the largest magnetic moments of all the 3+ rare earth cations, with paramagnetic moments of 9.72, 10.63, and 10.60 μ_B , respectively. With smaller radii than La³⁺ and Ce³⁺, these cations could preferentially substitute on different Yb sites. While this in itself may lead to different interactions with the magnetic Mn, the increased moments of these cations would likely result in much stronger interactions than previously observed. Solid solutions of Yb_{14-x}RE_xMnSb₁₁ (RE = Tb, Dy, Ho) have been prepared and their structure and magnetic properties measured.

2. Experimental

Single crystals of Yb_{14-x}RE_xMnSb₁₁ (RE = Tb, Dy, Ho) were grown using the Sn-flux method according to previously published optimized procedure for crystal growth [6, 10-12] with the elements in the molar ratio 14Yb : *p*RE : 6Mn : 11Sb : 86Sn (*p* was varied from 0.1-0.9 for each sample). The flux was removed from the crystals by centrifugation of the hot flux away from the crystals as described previously [6, 10-12]. A crystal from each reaction was mounted and polished followed by electron microprobe analysis using a Cameca SX-100 Electron Probe Microanalyzer with a wavelength-dispersive spectrometer. Elemental intensities for Yb, Mn, and Sb were determined relative to an Yb₁₄MnSb₁₁ single crystal standard and Tb, Dy, and Ho relative to their respective rare earth phosphate standards. 10 points of quantitative data was collected for each sample and converted to stoichiometric formulas by assuming 26 atoms per formula unit. Averages and standard deviations were calculated from this data. Back Scattered Energy (BSE) images of the crystals used for microprobe analysis and from other crystals from the same reactions are provided as Supporting Information. Small amounts of Sn flux inclusion or minor secondary phases can be seen in these large crystals.

Large single crystals of $p = 0.1$ and 0.5 for each series were fractured and small shards were mounted on a glass fiber and positioned under a 90 K nitrogen stream. Data were collected on a Bruker APEX CCD detector using graphite-monochromatic Mo $K\alpha$ radiation. The Bruker Apex suite was used for data collection, integration, and multi-scan absorption correction. Structure solutions were obtained using the SHELXTL 6.14 software package. Rare earth site occupancies were only refined for the $p = 0.5$ samples. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers (CSD) presented in Table 2.

DC magnetization data were obtained using a Quantum Design Magnetic Properties Measurement System (MPMS) superconducting quantum interface device (SQUID) equipped with a 7 T superconducting magnet. A single crystal which visually appeared to be flux free was mounted in a standard drinking straw using Kapton tape, with an attempt to orient the crystal close to the magnetic easy axis. Field-dependent magnetization data were collected at 5 K with the field ramped from 0 to 3 T, down to -3 T, and back up to 3 T. Temperature dependent magnetization data were obtained by cooling the samples to 5 K with no applied field applying a 100 Oe field, and collecting data from 5 to 300 K (zero-field cooled, ZFC), and then from 300 to 5 K (field cooled, FC). T_C were determined from a first order derivative. Several crystals were measured from each reaction to ensure reproducibility of results.

3. Results and discussion

Stoichiometric formulas of the $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ crystals used in this study were determined by electron microprobe analysis and are presented in Table 1. The preparative amount of RE used in the Sn flux synthesis, p , is provided along with the experimental formulas. Two samples of each rare earth containing composition were measured, one at low and the other at the highest RE substitution with the maximum solubility at $x \sim 0.5$. While samples synthesized with $p = 0.1$ RE trended towards $x = 0.2$ in the final product, samples made with $p \geq 0.3$ resulted in compositions around $x = 0.4 - 0.5$, with maximum compositions falling just below $x = 0.5$.

Table 1: Stoichiometric Formulas of Crystals as Determined by Electron Microprobe Analysis

RE_p	Stoichiometric Formula
Tb_{0.1}	Yb _{13.81(4)} Tb _{0.17(2)} Mn _{1.01(2)} Sb _{10.98(5)}
Tb_{0.3}	Yb _{13.56(7)} Tb _{0.40(2)} Mn _{0.96(2)} Sb _{11.05(8)}
Tb_{0.5}	Yb _{13.50(4)} Tb _{0.468(6)} Mn _{0.96(1)} Sb _{11.04(5)}
Tb_{0.7}	Yb _{13.49(4)} Tb _{0.47(1)} Mn _{0.96(1)} Sb _{11.04(4)}
Dy_{0.1}	Yb _{13.75(5)} Dy _{0.21(3)} Mn _{1.02(1)} Sb _{10.99(6)}
Dy_{0.5}	Yb _{13.51(4)} Dy _{0.48(4)} Mn _{1.02(2)} Sb _{10.96(5)}
Ho_{0.1}	Yb _{13.77(6)} Ho _{0.17(3)} Mn _{0.99(2)} Sb _{11.04(4)}
Ho_{0.5}	Yb _{13.50(4)} Ho _{0.44(1)} Mn _{0.99(2)} Sb _{11.04(4)}
Ho_{0.7}	Yb _{13.50(5)} Ho _{0.45(1)} Mn _{0.99(2)} Sb _{11.04(5)}

Single crystal X-ray diffraction (XRD) confirmed each compound to belong to the $Ca_{14}AlSb_{11}$ structure type in the $I4_1/acd$ space group [21]. The collection parameters are provided in Table 2. As shown in Figure 2, the lattice parameters increase with increasing RE content despite the fact that all three RE^{3+} cations are smaller than Yb^{2+} [22]. This same effect was observed with La, Ce, Pr, and Sm substitution, and it was suggested that the additional electron introduced by replacing an Yb^{2+} with a 3+ cation was responsible [10, 11, 23]. Small increases in some bond lengths and the $MnSb_4$ angle contributes to the increase in volume while the c/a ratio remains constant at ~ 1.32 . The size of the RE^{3+} cations decrease in the order Tb, Dy, Ho and, accounting for the amount of RE^{3+} , x . Figure 2 shows a consistent trend in volume vs six-coordination crystal radii [22]. While it is clear that for $RE^{3+} = Dy$ there is a deviation from the correlation, the specific reasons for why this is the case are not obvious.

Table 2: Single Crystal X-ray Diffraction Collection Parameters

RE_x^1	Tb _{0.17}	Tb _{0.47}	Dy _{0.21}	Dy _{0.48}	Ho _{0.17}	Ho _{0.44}
cryst dimensions (mm³)	0.073 x 0.075 x 0.120	0.094 x 0.115 x 0.146	0.070 x 0.089 x 0.113	0.057 x 0.074 x 0.100	0.066 x 0.067 x 0.089	0.053 x 0.067 x 0.072
x (XRD)²	0	0.40(1)	0	0.48(1)	0	0.5(1)
RE Sites	-	Yb(1)	-	Yb(1)	-	Yb(1) - 11(2)% Yb(4) - 1(2)%
Lattice params (Å)						
a	16.592(1)	16.600(2)	16.583(1)	16.611(3)	16.5847(6)	16.5845(6)
c	21.916(2)	21.963(3)	21.912(1)	21.966(5)	21.9167(8)	21.9411(8)
Max 2θ (deg)	30.486	30.656	27.468	30.593	30.500	30.501
no. of collected reflns	45166	45629	36681	36515	45289	45296
no. of unique reflections	2303	2349	1737	2334	2303	2304
μ Mo Kα (mm⁻¹)	52.936	52.474	53.004	52.403	52.983	52.690
R1 [I>2σ(I)]	0.0168	0.0173	0.0159	0.0214	0.0176	0.0175
wR2	0.0340	0.0354	0.0333	0.0424	0.0353	0.0321
Largest diff peak and hole (e Å⁻³)	1.153 -1.047	1.161 -1.177	1.126 -0.803	1.594 -1.294	1.310 -1.228	1.276 -1.260
CSD-number	430294	430250	430280	430254	430293	430252

¹RE_x indicates the appropriate RE (Tb, Dy, Ho) and x determined via microprobe.

²_x (XRD) indicates the amount of RE from the refinement of the single crystal data.

Figure 2: Unit cell volume vs RE six coordination crystal radius [22] for $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ (RE = Tb, Dy, Ho) from single crystal XRD. The compositions are indicated by RE_x. Ce-substituted data are from a previous single crystal study [11].

Single crystal refinement revealed that all three rare earths preferentially substituted on the 6-coordinated Yb(1) site, the smallest of the four crystallographically distinct Yb sites. In the case of Ho, a small amount also appeared to substitute on the Yb(4) site. The locations of the Yb(1) sites relative to the magnetic MnSb_4 tetrahedra is shown in Figure 3. Previous work on Ce-substituted $\text{Yb}_{14}\text{MnSb}_{11}$ determined that Ce preferentially substituted on the Yb(2) site followed by the Yb(4) site. The preference of Tb, Ho, and Dy for the Yb(1) site suggests that site preferences for rare earth substitutions in $\text{Yb}_{14}\text{MnSb}_{11}$ are determined by the size of cation, with smaller cations preferring the smallest site and larger cations preferring the largest. This is similar to the site preferences observed for $\text{Eu}_{14}\text{MnSb}_{11}$, although in that system Eu(3) is the preferred site for small cations, while none of the rare earths appear to substitute on Yb(3) in $\text{Yb}_{14}\text{MnSb}_{11}$ [24].

Figure 3: (a) The connectivity between the MnSb₄ tetrahedra (orange & blue) and the Yb(1) site (green). (b) Connectivity of Mn tetrahedral polyhedra with the pseudo-octahedral Yb(1) polyhedra.

Figure 4 shows the temperature dependent magnetization of Yb_{14-x}Tb_xMnSb₁₁ ($x = 0.17$ and 0.4) with inverse susceptibility vs temperature as an inset. The high temperature paramagnetic region is linear and can be fit to obtain a Weiss constant and an effective moment. In the paramagnetic region, the $x = 0.17$ sample has a moment of $6.1 \mu_B$, and the $x = 0.4$ sample has a moment of $8.0 \mu_B$, both close to their expected local moments of $(1-x) \text{Mn}^{2+}$, $x\text{Mn}^{3+}$ and $x\text{Tb}^{3+}$ (Yb²⁺ is closed shell f^{14} and therefore does not contribute). Both samples ferromagnetically order, with T_C of 47 K and 43 K for $x = 0.17$ and 0.4 respectively. The Weiss constant obtained from fitting the paramagnetic region is positive indicating ferromagnetic order and close to the observed transition temperature, T_C . The ZFC/FC susceptibility for $x = 0.17$ below the ferromagnetic ordering temperature splits right below the ferromagnetic transition and is complex below the Curie temperature, showing a transition at 10 K . In the case of the Tb $x = 0.4$ sample, just below the ferromagnetic ordering temperature the FC data increases up to a maximum at 5 K , while the ZFC decreases to a flat minimum below 15 K . A smaller split between ZFC and FC data was observed for Yb_{14-x}Tm_xMnSb₁₁ but at temperatures much lower than the onset of ferromagnetism [12]. This may suggest that the site preference of the RE^{3+} ion contributes to magnetic domains in a complex fashion. In contrast to Tm, where the site preference could not be distinguished by single crystal X-ray refinement, in the case of Tb, the majority of substitution is on the Yb(1) site. Figure 5 shows the field dependent magnetization for Yb_{14-x}Tb_xMnSb₁₁. While pristine Yb₁₄MnSb₁₁ does not show any coercive field [6], both these samples do, with coercive fields of about 20 Oe for $x = 0.17$ and 350 Oe for $x = 0.4$. The sample with $x = 0.17$ saturates at $5.2 \mu_B$ and the sample with $x = 0.4$ at $6.6 \mu_B$.

Figure 4: Temperature dependent susceptibility of $\text{Yb}_{14-x}\text{Tb}_x\text{MnSb}_{11}$ ($x = 0.17, 0.4$) at 100 Oe. Inverse susceptibility vs temperature is plotted in the inset.

Figure 5: Hysteresis loop of $\text{Yb}_{14-x}\text{Tb}_x\text{MnSb}_{11}$ ($x = 0.17, 0.4$) at 5 K.

Figure 6 shows the ZFC magnetization as a function of temperature of $\text{Yb}_{14.53}\text{Tb}_{0.47}\text{MnSb}_{11}$ for various applied fields. As the strength of the applied field increases, the spins align with the field at lower temperatures until at fields of 0.5 T and above, where increasing magnetization is no longer observed as temperature increases from 5 K. Higher fields also show a suppressed ferromagnetic transition. The fact that at low fields, the magnetic moment is very small and then increases can be attributed to domain wall pinning effect and the temperature dependence of the coercivity. The domain walls align below the ferromagnetic transition as the temperature is increased. Higher applied fields induce aligned moments at lower temperatures. Similar effects can be seen in susceptibility data for $\text{Yb}_{14-x}\text{Tm}_x\text{MnSb}_{11}$, where large applied fields suppress long range order [12].

Figure 6: ZFC temperature dependent magnetization for $\text{Yb}_{13.53}\text{Tb}_{0.47}\text{MnSb}_{11}$ with applied fields of 0.01, 0.05, 0.1, 0.5, 1, and 3 T.

Figure 7 shows the temperature dependent magnetization of $\text{Yb}_{14-x}\text{Dy}_x\text{MnSb}_{11}$ ($x = 0.21, 0.48$). In the paramagnetic region, the $x = 0.21$ sample has a moment of $7.2 \mu_B$ and the $x = 0.48$ sample $8.8 \mu_B$, both close to the expected values, assuming a similar model as above with $x\text{Dy}^{3+}$. Both compositions ferromagnetically order with T_C of 48 K for $x = 0.21$ and 44 K for $x = 0.48$. Below the ferromagnetic ordering temperature, the FC susceptibility increases to a maximum at 5 K and the ZFC data decreases to a minimum, flattening out below 15 K for $x = 0.21$ and 17.5 K for $x = 0.48$. Figure 8 shows the field dependent magnetization of $\text{Yb}_{14-x}\text{Dy}_x\text{MnSb}_{11}$ ($x = 0.21, 0.48$). Both compositions have a significant coercive field, with an H_C of approximately 500 Oe for $x = 0.21$ and 1000 Oe for $x = 0.48$. The saturation moment of $x = 0.21$ is $5.5 \mu_B$ and $x = 0.48$ is $7.4 \mu_B$.

Figure 7: Temperature dependent susceptibility of $\text{Yb}_{14-x}\text{Dy}_x\text{MnSb}_{11}$ ($x = 0.21, 0.48$) at 100 Oe. Inverse susceptibility vs temperature is plotted in the inset.

Figure 8: Hysteresis loop of $\text{Yb}_{14-x}\text{Dy}_x\text{MnSb}_{11}$ ($x = 0.21, 0.48$) at 5 K.

Figure 9 shows the temperature dependent magnetization of $\text{Yb}_{14-x}\text{Ho}_x\text{MnSb}_{11}$ ($x = 0.17, 0.45$). In the paramagnetic region, the $x = 0.17$ sample has a moment of $6.4 \mu_B$ and the $x = 0.45$ sample $8.6 \mu_B$, both close to their expected values. Both sample ferromagnetically order, with a T_C of 46 K for $x = 0.17$ and 41 K for $x = 0.44$. Below 30 K, the FC magnetization increases to a maximum and the ZFC magnetization decreases to a minimum, flattening out below 10 K in $x = 0.45$. Figure 10 shows the field dependent magnetization of $\text{Yb}_{14-x}\text{Ho}_x\text{MnSb}_{11}$. Both show a significant coercive field, with a H_C of 300 Oe for $x = 0.17$ and 400 Oe for $x = 0.45$. These compositions have saturation moments of $4.9 \mu_B$ for $x = 0.17$ and $7.9 \mu_B$ for $x = 0.45$.

Figure 9: Temperature dependent susceptibility of $\text{Yb}_{14-x}\text{Ho}_x\text{MnSb}_{11}$ ($x = 0.17, 0.44$) at 100 Oe. Inverse susceptibility vs temperature is plotted in the inset.

Figure 10: Hysteresis loop of $\text{Yb}_{14-x}\text{Ho}_x\text{MnSb}_{11}$ ($x = 0.17, 0.44$) at 5 K.

Table 3 shows a summary of the magnetic properties of the samples discussed above. χ_0 , C , and θ were determined by fitting the temperature dependent susceptibility above 100 K to the Curie-Weiss law. The effective moments, μ_{eff} , agree fairly well with the calculated moments assuming the RE substitutes as a 3+ cation and the additional electron fills the hole on the tetrahedron, reducing the screening of the Mn moments [11]. The calculated effective moments can be estimated by the equation $\mu_{\text{eff-calc}} = ((1-x)\mu_{\text{Mn(III)}}^2 + x\mu_{\text{Mn(II)}}^2 + x\mu_{\text{RE(III)}}^2)^{1/2}$ and are provided in Table 3. Effective moment values for the free ion of Tb, Dy, and Ho were used, 9.72, 10.63, and 10.60 μ_B , respectively [25]. Saturation moments are larger than that observed in $\text{Yb}_{14}\text{MnSb}_{11}$ which can be described as $\text{Mn } 3d^5 + h$, where the total saturation moment is 4 μ_B [6]. There are two ways to calculate the total saturation moment in the $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ compounds: (1) $\mu_{\text{sat-calc}} = ((1-x)4 \mu_B + x5 \mu_B + x\mu_{\text{sat(RE(III))}})$ or (2) $\mu_{\text{sat-calc}} = (4 \mu_B + x\mu_{\text{sat(RE(III))}})$. To calculate the total saturation moment, the gJ values of 7, 10, 10 μ_B are used for Tb, Dy and Ho [25]. In equation (1), the filling of the hole, h , by x increases the moment of Mn to 5 μ_B . In equation (2), Mn is still screened so that it is considered $3d^5 + h$ and is 4 μ_B . The best correlation between experiment and calculated saturation moment is found for equation (2) suggesting that the additional electron added to the $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ compounds does not increase the moment on Mn, but that the rare earth moment adds to the total moment. With the exception of $\text{Ho}_{0.17}$, the compositions containing low amounts of rare earths ($x = 0.17 - 0.21$) share approximately the same ordering temperature (T_C) of 48 K, reduced from the $\text{Yb}_{14}\text{MnSb}_{11}$ ordering temperature of 53 K, as previously seen with La, Tm, and Ce substitution [6, 10-12]. Due to the carrier mediated (RKKY) coupling, decreasing the carrier concentration by adding more rare earth should decrease the T_C further. The higher compositions of each rare earth have lower ordering temperatures than their corresponding lower compositions, but compared to each other they do not behave as expected. The Ho $x = 0.45$ sample has the lowest ordering temperature of 41 K, while the sample with the highest x of 0.48 (Dy) has an ordering temperature of 45 K, with the Tb $x = 0.4$ sample falling in between with a T_C of 43 K. The bifurcation of ZFC/FC can be attributed to anisotropy of the rare earth ion and formation of domain walls. Figure 11 compares the unit cell volumes determined by X-ray diffraction with T_C , showing the T_C of compositions with $x > 0.4$ increasing with cell volume. The effect of site substitution of the RE^{3+} ion along with the changing unit cell volume may provide changes in the exchange constants that leads to

the correlations observed. The only data point that does not appear to follow the trend of volume with respect to T_C is the Dy phase with $x = 0.21$.

Table 3: Magnetic Properties of $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ (RE = Tb, Dy, Ho)

RE	x	χ_0	C	θ	T_C (K)	H_C (Oe)	μ_{sat}	$\mu_{\text{sat-calc}}^1$	$\mu_{\text{sat-calc}}^2$	μ_{eff}^3	$\mu_{\text{eff-calc}}^4$
Tb	0.17	0.005(3)	6.1(6)	37(6)	47(1)	~20	5.2	5.4	5.2	7.0(3)	6.5(4)
Tb	0.4	0.0041(1)	7.97(3)	44.4(2)	43(1)	~350	6.6	7.2	6.8	7.98(2)	8.1(2)
Dy	0.21	0.0041(1)	5.14(3)	44.7(3)	48(1)	~500	5.5	6.3	6.1	6.41(2)	7.1(5)
Dy	0.48	0.011(1)	8.8(3)	43(2)	44(1)	~1000	7.4	9.3	8.8	8.4(1)	9.1(4)
Ho	0.17	0.0057(2)	5.81(6)	41.2(5)	46(1)	~300	4.9	5.9	5.7	6.81(4)	6.7(6)
Ho	0.45	0.0053(3)	8.63(7)	39.0(4)	41(1)	~400	7.9	9.0	8.5	8.30(3)	8.9(1)

$$^1 \mu_{\text{sat-calc}} = ((1-x)4 \mu_B + 5x \mu_B + x \mu_{\text{sat}}(\text{RE(III)}))$$

$$^2 \mu_{\text{sat-calc}} = (4 \mu_B + x \mu_{\text{sat}}(\text{RE(III)}))$$

$$^3 \mu_{\text{eff}} = (7.99C)^{1/2}$$

$$^4 \mu_{\text{eff-calc}} = ((1-x)\mu_{\text{Mn(III)}}^2 + x\mu_{\text{Mn(II)}}^2 + x\mu_{\text{RE(III)}}^2)^{1/2}$$

Figure 11: T_C vs unit cell volume determined by X-ray diffraction.

4. Conclusions

Single crystal X-ray diffraction and microprobe provide similar compositions for $\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ (RE = Tb, Dy, Ho). The unit cell volume increases with increasing amounts of a given RE^{3+} and, with the exception of Dy, decreases across the RE series as expected. This is attributed to small changes in the MnSb_4 tetrahedral bond length and angles. The RE^{3+} preferentially substitutes on the Yb(1) site which is the smallest volume Yb containing polyhedron. In the case of Ho^{3+} , a small amount of Ho^{3+} also substitutes on the Yb(4) site. In the paramagnetic region, the effective magnetic moments are consistent with the amount of substitution, x . In all samples, as x increases, the ferromagnetic ordering temperature, T_C ,

decreases. The saturation moment is consistent with x , $\text{Mn } 3d^5 + h$ and RE^{3+} . The coercive field increases with increasing x , and is largest for Dy and smallest for Tb. More detailed measurements of oriented single crystals are necessary to gain insight into the mechanism for ordering.

These are unique magnetic systems that can provide information concerning screening of the d moment via reduction of carrier concentration along with addition of f electrons. For the maximum x , there are still enough carriers for the RKKY mechanism to be valid in describing the ferromagnetic ordering and the RE moments contribute. The magnetic hysteresis is the first observed in the $\text{Yb}_{14}\text{MnSb}_{11}$ system, and relate to the strengths and anisotropy of the RE cations and how they order with the Mn.

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