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Supporting information

Single crystal growth and magnetic properties of the mixed valent Yb containing Zintl phase, $Yb_{14}MgSb_{11}$

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Experimental

Synthesis

Samples of $Yb_{14}MgSb_{11}$ were prepared by combining the elements, Yb (Ames Laboratory, with ≥ 99.9% purity), Mg pieces (Alfa Aesar, 99.95%), Sb shot (Alfa Aesar, 99.999%), Sn shot (Alfa Aesar, 99.99+%) were added in the ratio 14:6:11:95 to a 2ml alumina crucible with an alumina frit and empty catch crucible on top cushioned on top and bottom by silica wool and sealed under ¼ atm Ar in a fused silica tube. The sealed fused silica tube was placed upright into an alumina cup in a box furnace and heated from room temperature to 700 °C at a rate of 150 °C/h, dwelled at 700 °C for 1 h, then heated to 1000 °C at a rate of 150 °C/h, dwelled for 1 h and cooled to 750 °C over 125 h, at which temperature it was removed, inverted and centrifuged at max rpm for 10 seconds to remove the flux material. The growth crucible and frit were then separated to reveal shiny crystals with some remaining surface flux material. This optimized synthetic scheme results in a majority (>95%) of the main phase, tetragonal $Yb_{14}MgSb_{11}$, with small amounts of hexagonal Yb_5Sb_3, which can be readily identified and separated by morphology.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction was performed on small crystals cut to desired size under Paratone-N oil and mounted onto the diffractometer using MiTeGen micro loops. Data were collected under N_2 stream at 100 K on a Bruker Apex II diffractometer with CCD detector with Mo Kα radiation (λ = 0.70137 Å). The determination of the unit cell parameters, refinements, and raw frame data integrations were completed using the Bruker APEX II software. SADABS was used for absorption correction and SHELXS/SHELXL-2014/7 was used for solution and refinement.[1]

$Yb_{14}MgSb_{11}$ was first refined assuming full Yb occupancy of all sites and produced *R1/wR2* values of 0.0219/0.0305, with a *GooF* of 1.20, however there was residual density near Yb3 that was highlighted as an error during checkcif. Subsequent refinements allowed for Mg to refine on 1) all Yb sites, 2) Yb1,Yb2 and Yb3 only and 3) Yb1 and Yb3 only. The results are tabulated in Table s1.

The refinement chosen to be presented in the paper allowed Mg to refine on sites Yb1 and Yb3. While the differences in the R-values and goodness-of-fit values did not vary much from each model, this refinement did not exhibit the same residual density errors of the fully Yb-occupied model, and fit with both electron microprobe WDS data and prior reports of site specificity in this structure. Figure s1 details the occupancy percentages for this model and compares them to the corresponding average polyhedral bond length. Table s2 contains crystal data and refinement details not included in Table 1. CCDC 1854181 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table s1. Comparison of refinement models for $Yb_{14}MgSb_{11}$. The column label refers to each of the sites that Mg was allowed to refine on in each model.

	No Yb sites	**Yb1, Yb2, Yb3 and Yb4**	**Yb1, Yb2 and Yb3 only**	**Yb1 and Yb3 only**
R1 / wR2	0.0219 / 0.0305	0.0202 / 0.0233	0.0203 / 0.0237	0.0205 / 0.0245
GooF	1.20	1.24	1.23	1.22
Parameters	62	66	65	64
Greatest peak / hole ($e^-/Å^3$)	1.19 & -2.16	1.14 & -1.02	1.16 & -1.03	1.14 & -1.01
Amount of x In $Yb_{13-x}Mg_xMgSb_{11}$	0	0.30	0.22	0.15

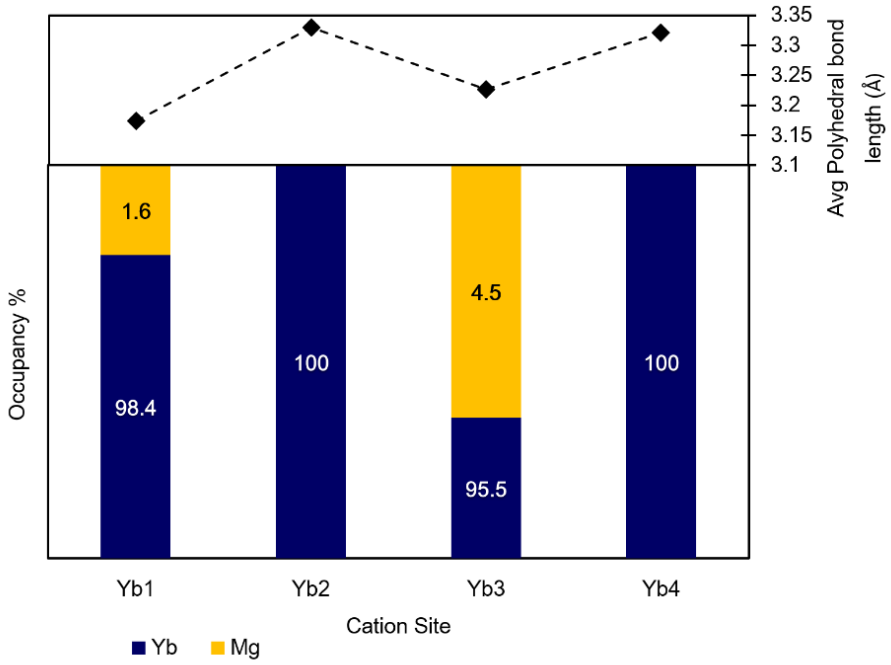

Figure s1. Refined percent occupancy of Yb and Mg as a function of cation site. Ytterbium is shown in blue and magnesium in gold. The average polyhedral bond length of each site is plotted in the line graph above percent occupancy.

Table s2. Selected crystal data and structure refinement details

Empirical formula	$Yb_{13.85}\ Mg_{1.15}\ Sb_{11}$
F(000)	12352.08
Crystal size	0.124 x 0.041 x 0.035 mm^3
Theta range for data collection	2.459 to 29.998°.
Index ranges	-23<=h<=23, -23<=k<=23, -31<=l<=31
Reflections collected	31164
Independent reflections	2224 [R(int) = 0.0408]
Completeness to theta = 25.242°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2224 / 0 / 64
Goodness-of-fit on F^2	1.224
Final R indices [I>2sigma(I)]	*R1* = 0.0170, *wR2* = 0.0241
R indices (all data)	*R1* = 0.0205, *wR2* = 0.0246
Extinction coefficient	0.0000156(4)
Largest diff. peak and hole	1.144 and -1.010 e.$Å^{-3}$

Electron Microprobe Analysis/ Wavelength Dispersive Spectroscopy

X-ray maps were obtained using a Cameca SX-100 electron microprobe at 15 kV and 20nA. A single crystal of $Yb_{14}MgSb_{11}$ set into epoxy and polished with a series of grits and sonicated in isopropanol between grit sizes until reaching an ultimate grit size of 0.05 µm. As the sample was somewhat air-sensitive, after polishing it was packaged under Ar and transported to the microprobe facility, where it was then immediately put under vacuum and carbon coated. Figure s2 is the backscatter image corresponding to the X-ray maps show in fig. Composition from WDS was obtained through an average over 20 points as shown in Figure s3. A single crystal of $Yb_{14}MnSb_{11}$ was used as the Yb standard. To obtain composition, Yb and Mg were standardized from Sb set to stoichiometric 11.00. Table s3 lists the average atomic percentage of each element obtained from WDS.

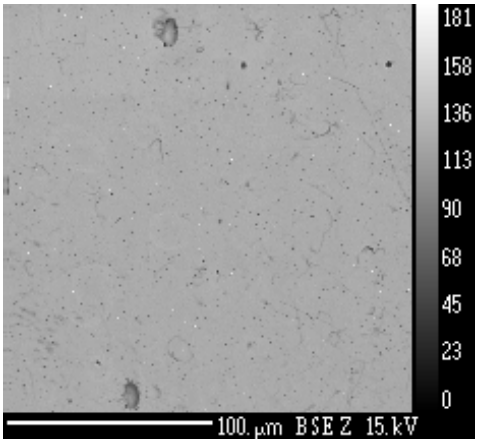

Figure s2. Backscatter electron image corresponding to the X-Ray maps in figure 2

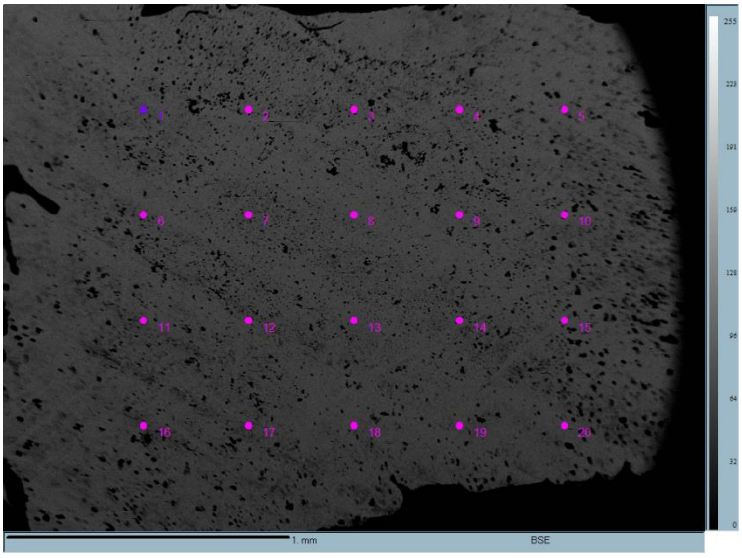

Figure s3. Backscatter electron image of $Yb_{14}MgSb_{11}$, with WDS quant points highlighted

Table s3. Average atomic % from 20 points taken on a polished single crystal of $Yb_{14}MgSb_{11}$ using wavelength dispersive spectroscopy.

	Yb	**Mg**	**Sb**
$Yb_{14}MgSb_{11}$ average atomic %	52.9(6)%	4.6(2)%	42.5(3)%

Magnetic Susceptibility

Magnetization data were acquired using a Quantum Design MPMS system under field of 10000 Oe from 300 K to 50 K with a step of 2 K, and from 50 K to 2 K with step of 1 K. Crystals selected for measurement were cleaned of excess flux material and mounted via sandwiching between 2 drinking straws. Crystals were found to decompose in dilute HCl, so Sn was removed from the outside of the crystal by scraping and by sanding faces until clean.

1. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.