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Synthesis, magnetism and electronic structure of $YbNi_{2-x}Fe_xAl_8$ ($x=0.91$) isolated from Al flux

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ABSTRACT

The combination of ytterbium, nickel, iron in liquid aluminum resulted in the formation of the new intermetallic compound $YbNi_{2-x}Fe_xAl_8$ ($x=0.91$) which adopts the $CaCo_2Al_8$ structure type with $a=14.458(3)$ Å, $b=12.455(3)$ Å, $c=3.9818(8)$ Å and space group *Pbam*. Its resistivity drops with decreasing temperature, saturating to a constant value at lower temperatures. Above 50 K, the inverse magnetic susceptibility data follows Curie–Weiss Law, with a calculated $\mu_{eff}=2.19\,\mu_B$. Although the observed reduced moment in magnetic susceptibility measurement suggests that the Yb ions in this compound are of mixed-valent nature, *ab initio* electronic structure calculations within density functional theory using LDA+*U* approximation give an f^{13} configuration in the ground state.

1. Introduction

Complex rare-earth aluminides are a growing class of intermetallics that has been identified predominantly through the application of metallic fluxes as a synthetic tool. Yb-based intermetallics display a variety of interesting physical properties such as mixed valency [1], super conductivity, heavy fermion [2] and Kondo-lattice behavior [3]. These characteristics are associated with the fact that the $4f^{13}$ and $4f^{14}$ electronic configurations of Yb are close in energy and they hybridize easily with the conduction electrons. In this sense, Yb is often considered as a $4f^{13}$ hole-analog to the Ce $4f^1$ electronic configuration. Ce-based intermetallic materials are more extensively studied, possibly because of the difficulty in synthesizing pure samples of Yb-based compounds associated with the high vapor pressure of Yb [4]. Ytterbium analogs have been successfully synthesized in the $RETM_2Tr_8$ system ($RE=$ rare earth, $TM=$ transition metal, $Tr=$ Al, Ga and In), along with Ce and Pr [5,6]. These compounds adopt the so-called $CaCo_2Al_8$ structure type. $CeFe_2Al_8$ is a rare example of a valence fluctuation compound containing Fe [7]. Mössbauer spectra indicate that the Fe atoms in $CeFe_2Al_8$ do not carry any magnetic moment [8]. $PrCo_2Al_8$ orders antiferromagnetically at 5 K, with a clear metamagnetic transition occurring at a critical field of 9000 G [9]. Several gallides adopting the $CaCo_2Al_8$ structure have also been reported, namely $REFe_2Ga_8$ ($RE=$ Ce, Pr, Nd, Sm) [10], $RECo_2Ga_8$ ($RE=$ Ce, Pr, Eu, Yb) [10,11] and $RERu_2Ga_8$ ($RE=$ La, Ce, Pr, Nd) [12], whereas $EuRh_2In_8$ was the first indide analog of this structure type [13].

The problem of high vapor pressure of ytterbium at high temperatures can be mitigated using flux synthesis, which is an effective method in exploring new material and obtaining high-quality single crystals [14]. Given the existence of $YbCo_2Al_8$ we explored the Yb–Ni–Fe–Al composition where the combination of Ni and Fe would be isoelectronic to two Co atoms. This led to the isostructural compound $YbNi_{2-x}Fe_xAl_8$ ($x=0.91$), which appears to be the first quaternary example reported in the $RETM_2Tr_8$ family.

Herein we describe the synthesis, crystal structure, physical properties and ^{57}Fe Mössbauer spectroscopy measurements of $YbNi_{2-x}Fe_xAl_8$ ($x=0.91$). In addition, we present detailed electronic structure calculations using *ab initio* density functional methods allowing for strong intra-site Coulomb repulsion for the *f* electrons giving rise to an f^{13} Yb^{3+} system [15–18].

2. Experimental section

2.1. Reagents

The following reagents were used as obtained: ytterbium (Cerac, 99.9%), nickel (99%, 325 mesh, Sargent, Buffalo Grove, IL),

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iron (99.99%, fine powder, Aldrich Chemical, Milwaukee, WI), aluminum (Cerac, 99.5%, −20 mesh).

2.2. *Synthesis*

Yb, Ni and Fe were mixed with excess Al in a nitrogen-filled glove-box. Alumina crucibles containing a mixture of 1 mmol of Yb metal (0.173 g), 1 mmol of Ni (0.059 g), 1 mmol of Fe (0.056 g) and 10 mmol of Al (0.270 g) were placed into silica tubes (13 mm o.d.), which were then sealed under vacuum ($\sim 10^{-4}$ Torr). The samples were heated to 1000 °C in 15 h, maintained at this temperature for 5 h, and cooled to 850 °C in 2 h. The mixtures were then annealed at 850 °C for 3 days, cooled to 500 °C in 35 h, and finally to room temperature in 10 h.

The excess aluminum was removed by soaking the crucible in aqueous 5 M NaOH solution overnight. The remaining crystalline product was rinsed with water and acetone. The major phase in the product was determined to be $YbNi_{2-x}Fe_xAl_8$ with a yield of 70–90%; while a small amount of $Yb_3Ni_5Al_{19}$ was also observed [19].

2.3. *Scanning electron microscopy and elemental analysis*

The crystals were selected and placed on a scanning electron microscope (SEM) sample plate using carbon tape. The chemical compositions of the products were determined by energy dispersive spectroscopy (EDS) performed on a JEOL JSM-35C SEM equipped with a NORAN EDS detector. Data were acquired by applying a 25 kV accelerating voltage with an accumulation time of 40 s. Typical crystals of $YbNi_{2-x}Fe_xAl_8$ feature needle morphologies as shown in Fig. 1. Over 20 crystals were analyzed with the resulting average elemental composition corresponding to the ratio of 1:1:1:8.

2.4. *X-ray crystallography*

Single-crystal X-ray diffraction data were collected for $YbNi_{2-x}Fe_xAl_8$ at room temperature on a Bruker AXS SMART CCD X-ray diffractometer. A data collection (Mo*K*α radiation, $\lambda = 0.71073$ Å) was acquired covering a full sphere of reciprocal space using exposure time 20 s/frame. The data acquisition and cell reduction were done with the SMART [20] software package and data processing was performed with the SAINTPLUS program [21]. An empirical absorption correction was applied to the data using the SADABS program [22]. The structure was solved using direct methods and refined with the SHELXTL package program [23]. Systematic absence conditions led to two possible space groups: *Pbam* and *Pba*2. The mean value of $|E^2 - 1|$ was 0.969 indicating that the structure was likely centrosymmetric. The centrosymmetric space group has a much lower combined figure of merit (CFOM) value and was found to be correct after final refinement.

In the structure of $YbNi_{2-x}Fe_xAl_8$, a total of 12 atomic sites including one Yb, two transition metal sites (Ni/Fe) and nine Al sites were identified. Originally the data was collected at 173 K covering a hemisphere of reciprocal space. Since the atomic numbers of Ni and Fe are very close to each other, different assignments on these two transition metal sites *M*(1) and *M*(2) were examined. Two satisfactory solutions were obtained: (a) the *M*(1) site was occupied by Ni and the *M*(2) was occupied by Fe with both sites fully occupied; (b) both *M* sites were occupied by a mixture of Ni/Fe: for *M*(1), Ni and Fe were found to have an occupation of 84.6% and 15.4%, respectively; while for *M*(2), the corresponding values were 33.5% and 66.5%. To further check this assignment, we collected single-crystal X-ray data covering a full sphere of reciprocal space. It was found that when the *M*(1) site was assigned to Ni and the *M*(2) site to Fe, the occupancy factors were 0.95 and 1.03, respectively, R_1 and wR_2 were 2.61% and 5.72%. If these two sites were switched, the occupancy factors were 1.06 and 0.94, R_1 and wR_2 values were 2.51% and 5.77%. As a result, the *M*(1) and *M*(2) sites were refined as mixed occupancy of Ni and Fe: 63%/37% on *M*(1) and 46%/54% on *M*(2) for Ni/Fe. This refinement gave the *R* values with R_1 2.52% and wR_2 3.95%. The resulting stoichiometry is in agreement with the elemental analysis from EDS. Data collection parameters and refinement details for $YbNi_{2-x}Fe_xAl_8$ are shown in Table 1. Atomic positions and occupancies are listed in Table 2.

The X-ray powder diffraction data were collected at room temperature on a CPS 120 INEL X-ray diffractometer (Cu*K*α) equipped with position-sensitive detector. Experimental powder patterns were compared to the patterns calculated from the single-crystal structure solution (by the CrystalDiffract program [24]) to assess phase identity and purity.

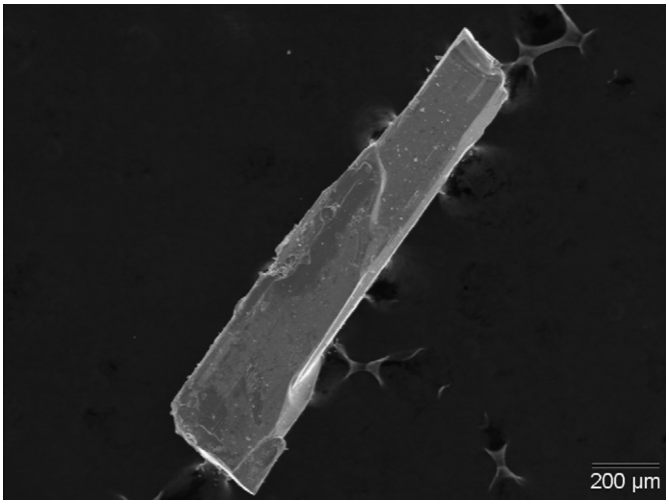

Fig. 1. SEM image of a typical crystal of $YbNi_{2-x}Fe_xAl_8$ grown from aluminum flux.

Table 1
Selected crystal data and structure refinement details for $YbNi_{2-x}Fe_xAl_8$

Empirical formula	$YbNi_{2-x}Fe_xAl_8$
Formula weight	503.44
Crystal system	Orthorhombic
Space group	*Pbam* (#55)
Unit cell dimensions	$a = 14.458(3)$ Å
	$b = 12.455(3)$ Å
	$c = 3.9818(8)$ Å
Volume	717.1(2) Å^3
Z	4
Density (calculated)	4.663 Mg/m^3
Absorption coefficient	18.404 mm^{-1}
F(000)	912
Crystal size	$0.22 \times 0.30 \times 0.24$ mm^3
θ range for data collection	2.82–27.79°
Limiting indices	$-16 \leqslant h \leqslant 16$
	$-19 \leqslant k \leqslant 18$
	$-5 \leqslant l \leqslant 5$
Reflections collected	6852
Independent reflections	929 [$R_{int} = 0.0275$]
Completeness to $\theta = 37.00°$	95.6%
Data/restraints/parameters	929/0/72
Goodness-of-fit on F^2	1.056
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0252$, w$R_2 = 0.1041$
R indices (all data)	$R_1 = 0.0259$, w$R_2 = 0.1052$
Largest diff. peak and hole	2.316 and −1.497 e Å^{-3}

$$R_1 = \sum(|F_o| - |F_c|) \Big/ \sum |F_o|; \quad wR_2 = \left\{ \sum \left[w(F_o^2 - F_c^2) \right] \Big/ \left[\sum (w|F_o|^2)^2 \right] \right\}^{1/2}.$$