



Neutron powder diffraction, and solid-state deuterium NMR analyses of Yb_2RuD_6 and spectroscopic vibrational analysis of Yb_2RuD_6 and Yb_2RuH_6

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ABSTRACT

The crystal structure of Yb_2RuD_6 has been determined by neutron powder diffraction and the results were consistent with the $Fm\bar{3}m$ (#225) space group, $a=7.2352(18)$ Å, with the atoms arranged according to the well-known K_2PtCl_6 structure. No structural phase transition was observed in going from room temperature to 4 K. Raman spectra were not available due to fluorescence, but all fundamental bands and combination bands were assigned from FTIR and PAIR spectra only following previous studies for other alkaline earth and europium ruthenium ternary metal hydrides and deuterides. The deuterium nuclear quadrupole coupling constant, 40.9 kHz, leads to an ionic character of the Ru–D bond of 82%.

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1. Introduction

As attractive as hydrogen is as a viable alternative energy source to replace current fossil fuels several challenges have yet to be overcome before it is adopted widely. One of these challenges is the storage of hydrogen. Hydrogen–metal complexes are one class of materials that have sparked an interest as a potential storage system [1]. Usually aimed at compounds of light weight and relatively inexpensive metals the goal has been towards maximizing the gravimetric hydrogen density. However, complexes of heavier transition metals can have high volumetric hydrogen densities and this has led to considerable research on, for example, ternary metal hydrides (TMH) of the Group 8 elements of the general formula $A_2\text{MH}_6$ where $M=\text{Fe, Ru and Os}$ and A = either an alkaline earth element or Eu and Yb. The preparation, unit cell dimensions and properties of Yb_2RuH_6 were first reported in the mid-1970s [2,3]. The structure was based only on powder X-ray diffraction of the hydride. In addition, it was reported that the compound was diamagnetic, consistent with divalent Yb and a divalent Ru with a low spin $4d^6$ electronic configuration. Also, the temperature dependent electrical resistivity measurements were consistent with semiconductor behavior. Only the infrared active Ru–H symmetric stretching and bending modes were reported [3]. Since that time the vibrational

analyses of TMHs by IR, Raman and inelastic neutron scattering have matured greatly. For any analysis to be complete, the interatomic distances of the transition metal–hydrogen (deuterium) must be known. That requires the application of neutron diffraction, to fully elucidate any structure. Thus, we report the results of the complete structure of Yb_2RuD_6 and vibrational analysis of Yb_2RuH_6 and Yb_2RuD_6 .

The current state of the spectroscopic properties of ternary metal hydrides has been reviewed recently by Parker [4]. All of the compounds adopt the K_2PtCl_6 structure. The fifteen vibrational spectroscopic modes of the isolated octahedral (O_h) complex anion, i.e. $[\text{MH}_6]^{4-}$, are limited to three Raman, two infrared active and one inactive mode due to the high symmetry. In the observed spectrum there are additional peaks due to combination bands which, due to the selection rule that these bands must arise from a g- and u-mode combination, appear only in the infrared spectrum. In previous studies on Ca_2RuH_6 and Sr_2RuH_6 [5] the inelastic neutron scattering (INS) spectra were obtained. This method has the advantage that there are no selection rules and all vibrations appear in the spectrum, including the inactive modes, combination bands and overtones. Thus, it was possible to analyze fully the spectra and assign all the peaks in both compounds. In the case of the europium compound, due to the high neutron absorption of the europium, it was not possible to obtain the INS spectrum. Nevertheless it was still possible to complete the assignments.

The properties of these Group 8 TMHs, while strongly dependent on the transition metal, show that the counter-ion also plays

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a significant role and an investigation of the structure and spectroscopic properties of a second lanthanide complex, Yb_2RuH_6 (D_6), is reported. The analysis of the vibrational spectra represented an unusual problem in that the presence of Yb_2O_3 impurity caused high fluorescence upon laser irradiation and prevented observation of the Raman spectra. Thus, the determination of the wavenumbers of all the fundamentals had to be based on infrared spectra only.

In addition, the deuterium nuclear quadrupole coupling constant has been measured by solid state NMR in order to obtain the ionic character of the Ru–D bond.

2. Experimental

Yb_2RuH_6 and Yb_2RuD_6 were prepared as described previously, i.e. purification of the Yb metal, formation of the Yb binary hydride/deuteride and the high temperature gas/solid phase reaction of the ternary metal compound [2]. One change was incorporated. The powder X-ray diffraction pattern of the ternary metal product revealed, in addition to the product phase, some unreacted binary metal deuteride/hydride, ruthenium and an oxide impurity. The product powder was repelletized and reheated at 800 °C in approximately one atmosphere of deuterium (hydrogen). This reheat resulted in a decrease in the amount of starting materials as judged by powder X-ray diffraction analysis (PXRD). A second reheat resulted in the disappearance of the binary ytterbium deuteride (hydride), a small amount of ruthenium, some Yb_2O_3 impurity and much sharper diffraction lines of the TMD or TMH as judged by PXRD analysis.

Neutron powder diffraction (NPD) data were collected using the 32 detector BT-1 neutron powder diffractometer at the National Institute of Standards and Technology (NIST), Center for Neutron Research Reactor (NBSR). Measurements were made at 4 K and room temperature (295 K) between 2θ values of 10° and 160° using a wavelength of 1.5403 Å [1]. The neutron data were fit using Rietveld analysis [6] and the GSAS and EXPGUI programs [7,8]. The starting structural model was taken from previous results [2]. The structure of Yb_2RuD_6 was modeled with one variable coordinate and independent isotropic displacement parameters for each atom type. To model the expected incomplete isotopic exchange, both D and H atoms were placed at the $(x,0,0)$ positions and constrained to have total occupancy of unity. The background was fit with an 8-term Chebyshev polynomial but was fixed in the final 4 K refinements, due to correlation with the U_{iso} values. The GSAS type 3 profile with the Finger–Cox–Jephcoat low angle symmetry was used [9].

Infrared spectra were scanned with a Thermo Nicolet Avatar Model 370 FTIR instrument over a range of 4000–400 cm^{-1} . Samples were prepared in IR grade KBr matrices. Photo-acoustic infrared (PAIR) spectra were recorded using a Bio-Rad FTS6000 spectrometer equipped with a MTEC 300 PA detector in rapid scan mode at 4 cm^{-1} resolution.

NMR spectra were acquired using a Varian 400 MHz spectrometer operating at 61.4 MHz for deuterium resonance with a $90^\circ\text{--}\tau\text{--}90^\circ$ sequence with a 90° pulse width of 43 μs , τ of 30 μs , recycle delay of 150 s and 136 repetitions.

3. Results and discussion

Table 1 contains the refinement agreement and structural parameters for Yb_2RuD_6 . The fits for the room temperature and low temperature data sets are shown graphically in Fig. 1(a) and (b), respectively. The peaks exhibited some additional Lorentzian (LY) strain broadening, but the Gaussian parameters

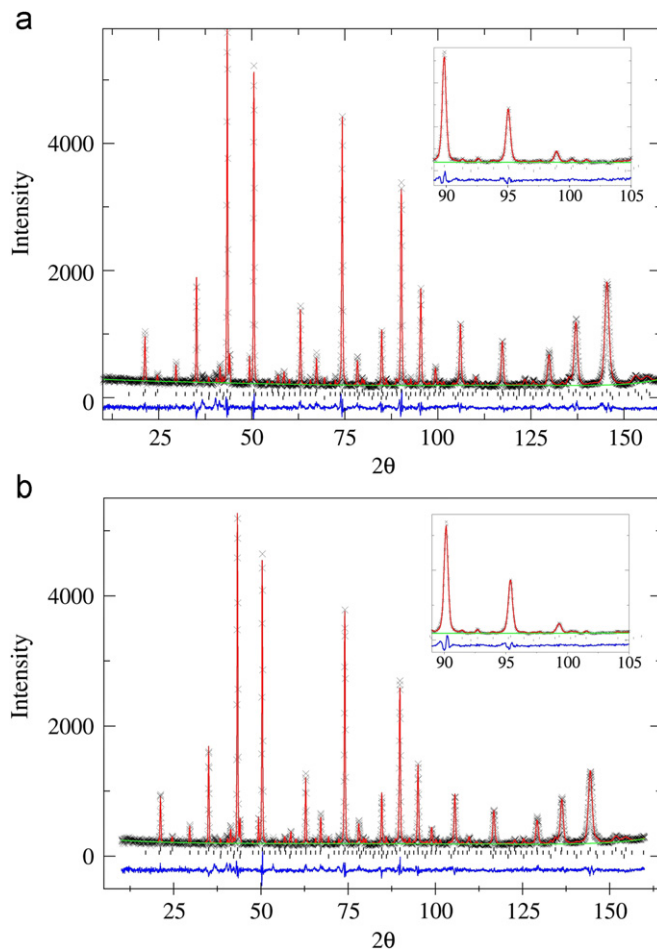


Fig. 1. Observed (continuous line) and calculated (crosses) neutron powder diffraction data for Yb_2RuD_6 at (a) 295 K and (b) 4 K. The difference curve ($I_{\text{obs}} - I_{\text{calc}}$) is shown at the bottom. A magnified portion of the fit is shown in the upper right side. The short vertical lines indicate positions of allowed reflections (from top) for the title compound, Yb_2O_3 and Ru impurities.

Table 1
Neutron diffraction structural results for Yb_2RuD_6 . Fractional coordinates for space group $Fm\bar{3}m$ are Yb (8c, $-43m$) $x=y=z=1/4$, Ru ($4a$, $m\bar{3}m$) $x=y=z=0$ and D ($24e$, $4m\bar{m}$); x listed in the table and $y=z=0$.

T (K)	a (Å)	x(D) (frac.)	U_{isoRu} (Å ²)	U_{isoYb} (Å ²)	U_{isoD} (Å ²)	
4	7.2157(18)	0.2387(3)	−0.0007(4)	0.0022(2)	0.0139(3)	
295	7.2352(18)	0.2374(2)	0.0022(4)	0.0073(3)	0.0195(4)	
T (K)	Ru–D (Å)	Ru–Yb (Å)	Yb–D (Å)	R_{wp} (%)	R_f (%)	χ^2
4	1.7223(19)	3.12450(3)	2.55245(6)	7.80	4.2	2.15
295	1.7180(19)	3.13293(3)	2.55964(7)	7.20	3.2	1.63

matched the native instrumental resolution. The percent isotopic purity level for deuterium was 97.2(5) and 98.2(5) for the low and high temperature analyses, respectively, close to the detection limit. Impurity peaks from Yb_2O_3 and unreacted Ru were apparent in the pattern and were modeled by addition of those phases to the refinement. From these data the mass impurity abundance levels were calculated at 8.9(5)% and 7.6(4)% for Ru and 6.0(2)% and 6.5(2)% for Yb_2O_3 at 4 and 295 K, respectively. A very few small peaks from another phase were also present but this phase could not be identified. The results are consistent with other similar, six coordinate, TMHs, i.e. Yb_2RuD_6 adopts the K_2PtCl_6 structure and does not undergo a phase transition to lower symmetry in going from room temperature to temperatures approaching 4 K. The length of the unit cell 7.2352(18) Å agrees with 7.248 Å reported earlier for Yb_2RuH_6 (2).

The PAIR and FTIR spectra for Yb_2RuH_6 and Yb_2RuD_6 are shown in Figs. 2 and 3, respectively. The wavenumbers of the peaks observed in the FTIR and PAIR spectra along with their respective vibrational assignments are found in Table 2. The symmetry requirements allow only two infrared active modes. The very strong peaks at 1548 cm^{-1} for the TMH and 1110 cm^{-1} for the TMD are easily assigned to the Ru–H(D) asymmetric

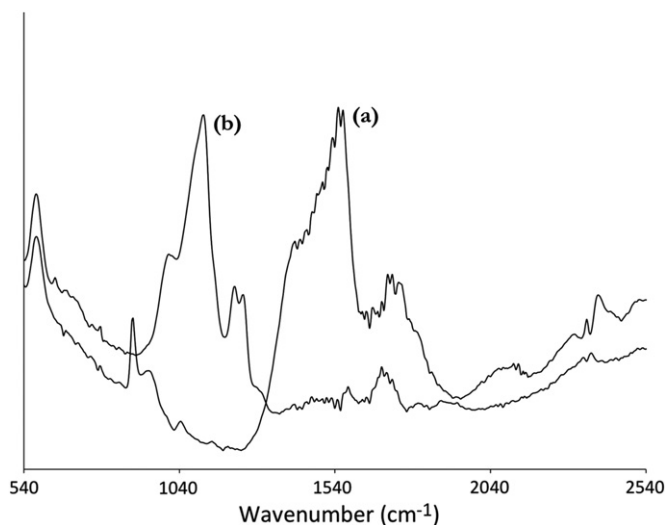


Fig. 2. Vibrational PAIR spectra of (a) Yb_2RuH_6 and (b) Yb_2RuD_6 .

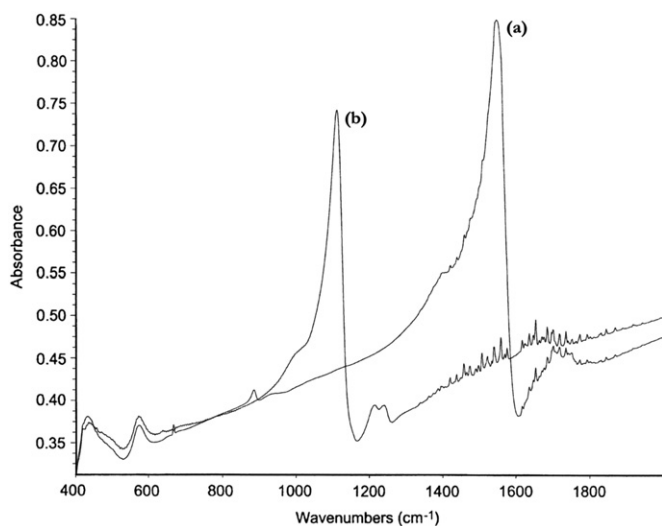


Fig. 3. Vibrational FTIR spectra of (a) Yb_2RuH_6 and (b) Yb_2RuD_6 .

Table 2
Observed wavenumber (cm^{-1}) and assignments for Yb_2RuH_6 and Yb_2RuD_6 .

Yb_2RuH_6	Yb_2RuD_6	Assignment
2719	1927	$\nu_1 + \nu_4$
2621	1883	$\nu_2 + \nu_4$
2299	1632	$\nu_2 + \nu_{\text{LIB}}$
1728	1241	$\nu_4 + \nu_5$
1699	1215	$\nu_5 + \nu_6$
1412	1009	$\nu_6 + \nu_{\text{LIB}}$
1548	1113	ν_3
886	636	ν_4

Table 3
Derived wavenumbers of fundamentals for Yb_2RuH_6 and Yb_2RuD_6 . (Note ν_3 and ν_4 are observed.)

Fundamental	H	D
ν_1	1833	1307
ν_2	1740	1241
ν_3	1548	1110
ν_4	886	636
ν_5	847	604
ν_6	852	607
ν_{LIB}	560	399

stretch, ν_3 , and the peaks 886 cm^{-1} for the TMH and 636 cm^{-1} for the TMD to the bending mode, ν_4 . In the absence of the Raman spectra, these are the only two peaks directly observed, but, as shown in a previous study of $\text{TMH}(\text{D})\text{s}(5)$, $\text{Ca}_2\text{RuH}_6(\text{D}_6)$ and $\text{Sr}_2\text{RuH}_6(\text{D}_6)$, the peaks on either side of the ν_3 absorption are known to be the combination bands $\nu_6 + \nu_{\text{LIB}}$, $\nu_5 + \nu_6$ and $\nu_4 + \nu_5$. Thus, it was possible to derive values for ν_5 , ν_6 and ν_{LIB} , the latter two being inactive fundamentals. Combination bands at higher wavenumbers were assigned to $\nu_1 + \nu_4$ and $\nu_2 + \nu_4$ and this allowed for the further derivation of the other two Raman allowed modes. The wavenumbers of the modes for the TMD were used as confirmation. The derived wavenumbers for the TMH and TMD fundamentals are shown in Table 3. The wavenumber ratios were consistent at 1.402, i.e. very close $\sqrt{2}$. Thus, with only two observable fundamentals it was possible to use combination bands to derive the Raman fundamentals, the inactive modes and the vibrational modes. In comparing the wavenumbers of the fundamentals of the two lanthanide salts, i.e. Yb and Eu, all fundamentals are higher for the Yb salt, except for the vibrational mode. The absorption peaks below 600 cm^{-1} are assigned to Yb_2O_3 [10].

The static deuterium NMR spectrum showed a splitting of the “horns” of the Pake-doublet, which was equivalent to a nuclear quadrupole coupling constant, C_Q , of 40.9 kHz. This value can be interpreted in terms of the percent ionic character of the Ru–D bond of 82%, which is larger than that found for Ca_2RuD_6 of 76% [11,12]. This difference is consistent with the Ru–D bond length decreasing from 1.7224 Å for the Yb(TMD) to 1.7200(2) Å for the Ca(TMD).

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