

Synthesis and Structures of $[\text{Sr}_{2-x}\text{Eu}_x]\text{IrH}_5$, $[\text{Sr}_{2-x}\text{Eu}_x]\text{RhH}_5$, $[\text{Ca}_{2-x}\text{Eu}_x]\text{IrH}_5$, and Eu_2RhH_5

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Samples of various compositions of $[\text{Sr}_{2-x}\text{Eu}_x]\text{MH}$ where $M = \text{Rh}$ or Ir and $[\text{Ca}_{2-x}\text{Eu}_x]\text{IrH}_5$ were synthesized from stoichiometric mixtures of EuH_2 , SrH_2 , or CaH_2 , and Rh or Ir powders in a hydrogen atmosphere at 700°C . Powder X-ray diffraction data of the black single-phase products were indexed on the basis of a face-centered cubic lattice. The variations in the unit cell parameters as a function of x were consistent with Vegard's Rule for $0 \leq x \leq 2$ range. The unit cell parameters increased with decreasing x between the limits of 7.580 and 7.651 Å for $[\text{Sr}_{2-x}\text{Eu}_x]\text{IrH}_5$ and between the limits of 7.557 and approximately 7.60 Å for $[\text{Sr}_{2-x}\text{Eu}_x]\text{RhH}_5$. Unit cell parameters increased from 7.297 to 7.580 Å as x went from 0.25 to 2 for $[\text{Ca}_{2-x}\text{Eu}_x]\text{IrH}_5$. The estimated standard deviation for the unit cell parameters is 0.001 Å. The crystal structures belonged to the $Fm\bar{3}m$ (No. 225) space group with random occupancy of Sr or Ca and Eu in the $8c$ sites, Rh or Ir ions located at the $4a$ sites, and H in the $24e$ sites. The formation of Eu_2RhH_5 is also reported. The X-ray diffraction data for this new ternary hydride were indexed FCC with the cell length equal to 7.555 Å. © 1996 Academic Press, Inc.

1. INTRODUCTION

Mixed crystal quaternary metal hydrides, QMHs, of the type discussed in this paper are systems wherein the properties vary regularly with changes in composition. We have reported previously the preparation, structure, and magnetic behavior for $[\text{M}_{2-x}\text{Eu}_x]\text{RuH}_6$ where $M = \text{Ca}$ or Sr (1, 2). It has been shown that the alkaline earth ions and the europium ions are completely miscible. The unit cell parameter changes linearly with x and obeys Vegard's Rule.

The hydride chemistry of europium is restricted to divalent europium. Furthermore, europium has the interesting characteristic of conferring ferromagnetic behavior on its binary hydride and in its few ternary metal hydrides, TMHs, and mixed crystal QMHs (3–6). The mixed crystal quaternary systems alluded to above lend themselves well to an understanding of the behavior of the exchange cou-

pling constants. Based on paramagnetic Curie Weiss constants the results so far appear to suggest that the exchange coupling constants depend on the nearest neighbor europium cation separation.

This paper presents the results of experiments designed to prepare similar mixed crystal systems with the Group IX rarer platinum metals rhodium and iridium and to examine their crystal structures by X-ray powder diffraction analysis. Preliminary results have been reported (7). An outgrowth of this work was the formation of a new ternary hydride, Eu_2RhH_5 , which was found to be isostructural with Eu_2IrH_5 (5).

2. EXPERIMENTAL

The three-step procedure used to prepare the mixed crystal QMHs has been previously reported (1, 2). Briefly it consisted of (1) purifying the calcium, strontium, and europium metals as received by high temperature vacuum distillation, (2) forming the binary hydrides of the purified metals in (1) by direct combination of the elements, and (3) preparing the QMHs by heating the binary hydrides of choice with rhodium or iridium metal at 700°C in approximately 700 Torr of hydrogen. A typical experiment in step (3) might require 15 minutes to go from room temperature to 700°C , then heated for approximately 15–20 hours at 700°C , and finally cooled quickly to room temperature by sliding the furnace away from the sample chamber.

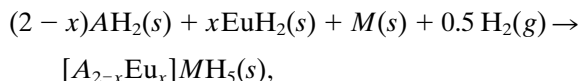
X-ray powder diffraction patterns were obtained using a Philips Model 1840 diffractometer. An internal standard of silicon powder purchased from the National Institute of Science and Technology was used to measure accurately the Bragg angles. Nickel filtered copper $K\alpha$ radiation was used. The samples were prepared for X-ray scanning by smearing the powder sample with petroleum jelly on to the surface of a modified glass microscope slide. All samples were scanned from 2θ of 12° to 120° using a goniometer speed of $0.005\ 2\theta/\text{s}$ and a chart speed of $50\ \text{mm}/^\circ 2\theta$. The experimental intensities were determined by measur-

ing the area under the diffractometer tracings with a planimeter. The INTENSE computer program (8) was used to calculate the intensities.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The formation of the QMHs can be represented by the equation



where A is Ca or Sr and M is Rh or Ir. Values of x were 0, 0.25, 0.5, 1.0, 1.5, 1.75, and 2.00.

Hydrogen was absorbed during the reactions by noting a decrease in the pressure. The products were all single-phase polycrystalline black solids which were reactive to water slightly acidified with 6 M HCl. It has been established for TMHs of the Group IX metals of this type that approximately 0.5 moles of hydrogen are taken up per mole of noble metal (9, 10). This behavior results in a stoichiometry which is consistent with the rule of 18 or the effective atomic number for rhodium and iridium. For this work, we assumed that the amount of hydrogen absorbed would be consistent with this rule.

3.2. Crystal Structure for $[Sr_{2-x}Eu_x]IrH_5$,

$[Sr_{2-x}Eu_x]RhH_5$, and $[Ca_{2-x}Eu_x]IrH_5$

All the powder X-ray diffraction patterns were indexed on the basis of a face-centered cubic symmetry.

Complete miscibility between strontium or calcium and europium was observed. The change in the unit cell size with changes in the composition of the mixed crystal systems obeyed Vegard's Rule. The rule implies that the changes are governed purely by the relative sizes of the ions that replace each other in a simple substitutional mechanism, i.e., $Ca^{+2}(1.14 \text{ \AA})$ or $Sr^{+2}(1.32 \text{ \AA})$ for $Eu^{+2}(1.31 \text{ \AA})$ (11). The unit cell parameters for the different compositions are given in Table 1.

TABLE 1
Unit Cell Lengths (Å)

x	$[Sr_{2-x}Eu_x]IrH_5$	$[Sr_{2-x}Eu_x]RhH_5$	$[Ca_{2-x}Eu_x]IrH_5$
0	7.651		
0.25	7.636	7.602	7.297
0.50	7.630	7.594	7.340
1.0	7.610	7.591	7.429
1.5	7.595	7.569	7.563
1.75	7.588	7.568	
2.00	7.580	7.557	7.580

Note. ESD = 0.001 Å.

Figure 1 displays plots of the unit cell parameters versus x and the graphs appear to be linear in form. Linear regression analyses on the data in Table 1 are give below. For $[Sr_{2-x}Eu_x]IrH_5$ the equation is

$$a = -0.03307x + 7.645,$$

where a is the unit cell parameter. The predicted value of 7.645 Å is in close agreement with experimental value of 7.651 Å for the unit cell parameter of Sr_2IrH_5 (12). For $[Sr_{2-x}Eu_x]RhH_5$ the equation is

$$a = -0.02338x + 7.608.$$

The 7.608 Å value is in close agreement with the experimentally observed value of 7.60 Å reported for Sr_2RhH_5 (9). For $[Ca_{2-x}Eu_x]IrH_5$ the equation is

$$a = 0.1748x + 7.258.$$

Again, the 7.258 Å value agrees with the experimentally reported value of 7.29 Å for Ca_2IrH_5 (9).

The $Fm\bar{3}m$ (No. 225) space group was assigned to the QMH structures. The structure assignment is based on the well-known K_2PtCl_6 (see Fig. 2) structure which has been successfully applied to structures of the high-temperature phase of the alkaline earth TMHs with cobalt, rhodium, and iridium (10, 12, 13). The calcium or strontium and the europium ions were assigned to the eightfold sites (larger speckled spheres), i.e., $8c$ (1/4, 1/4, 1/4 and 3/4, 3/4, 3/4) assuming random occupancy. Rhodium or iridium ions were located at the four fold sites (smaller black spheres), i.e., $4a$ (0, 0, 0). Hydrogens were assigned randomly to 20 of the 24-fold sites (vertices of the octahedra), i.e., $24e$ ($\pm x, 0, 0; 0, \pm x, 0; 0, 0, \pm x$) with $x = 0.25$. Neutron diffraction studies for M_2IrD_5 where $M = Sr$ or Eu placed x equal to approximately 0.22 (12, 14).

Intensities were calculated for each of the compositions given in Table 1. Typical results are given in Table 2 for compositions $[Sr_{2-x}Eu_x]IrH_5$, $[Sr_{2-x}Eu_x]RhH_5$, and $[Ca_{2-x}Eu_x]IrH_5$ where $x = 1$.

The positions of the H(D) have yet to be assigned with certainty by powder neutron diffraction experiments. As noted previously it has been shown that Sr_2IrD_5 adopts the well-known K_2PtCl_6 structure with the H(D) having a sixfold disordered high-temperature structure and a twofold ordered low-temperature phase (12). The H(D) occupy the $24e$ sites ($\pm x, 0, 0$) ($0, \pm x, 0$); ($0, 0, \pm x$) where x is approximately 0.224. It is suspected that once the entire structure has been completed the H(D) will take up similar positions in the QMHs. It should be noted, however, that no order/disorder behavior was detected for Eu_2IrD_5 from 9 K to room temperature (14). With both Sr and Eu in these mixed crystal

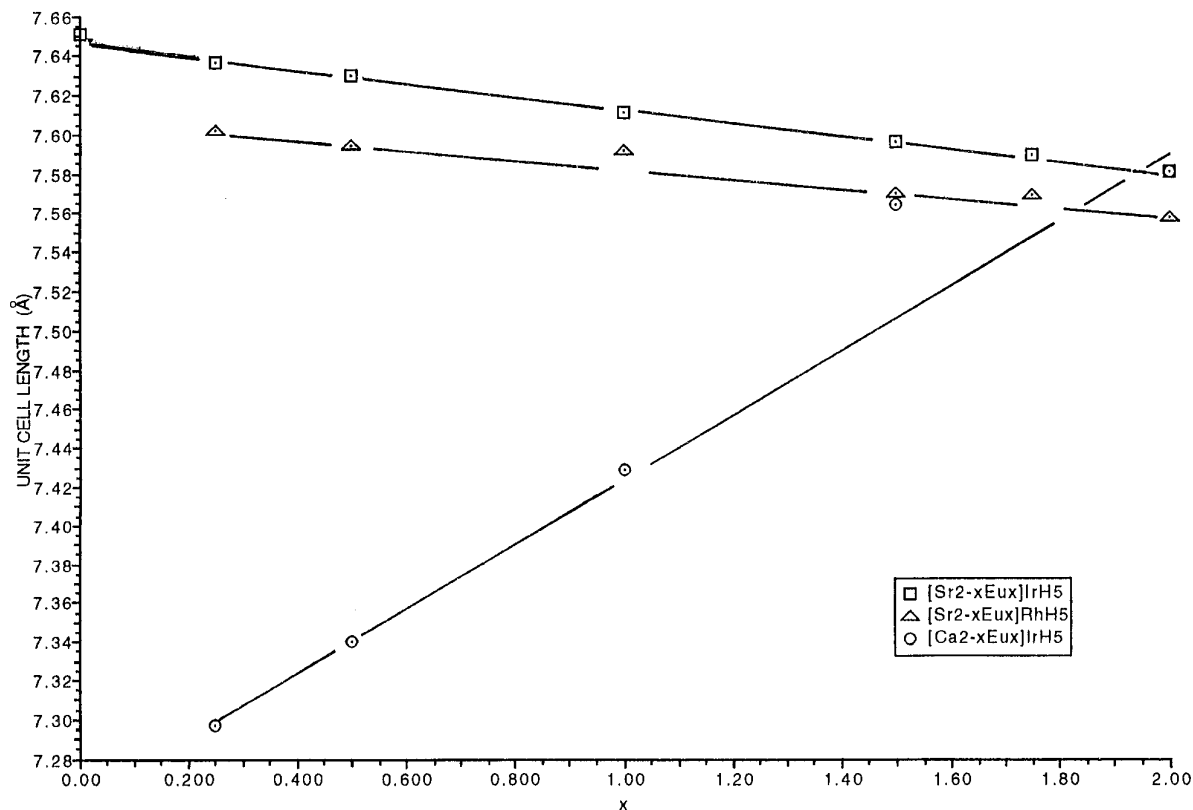


FIG. 1. Unit cell parameter (Å) versus x .

systems it would be interesting to ascertain whether a temperature dependent phase change is observed over the entire composition range of the QMHs.

The magnetic behavior for $[\text{Sr}_{2-x}\text{Eu}_x]\text{IrH}_5$ where $x =$

0.5, 1.0, 1.5, and 2.0 has been studied. Measurements were made by the Faraday body force method at temperatures from 10 K to room temperature and at magnetic fields from 200 to 8350 Gauss. Preliminary results for the Curie temperatures, Weiss Curie constants, and magnetic moments are reported in Table 3 (15). As a reference the magnetic susceptibility of Sr_2IrH_5 at 295 K is 1.5×10^{-4} emu/mole. The complete work will be published later.

The magnetic moments are consistent with divalent europium which has a calculated value of 7.94 BM. A "hint" of Eu_2O_3 is observed in the X-ray powder diffractograms and is undoubtedly responsible for the suppressed moments seen in Table 3.

Ferromagnetic Curie temperatures were observed or estimated for all the europium containing samples. The data show that T_c decreases as the presumed number of nearest neighbor Eu^{2+} ions decrease. This decrease in T_c suggests a decrease in the strength of the nearest neighbor exchange interactions.

3.3. Synthesis and Structure of Eu_2RhH_5

As part of the $[\text{Sr}_{2-x}\text{Eu}_x]\text{RhH}_5$ study, Eu_2RhH_5 was prepared, i.e., where $x = 2$. This new TMH was formed at

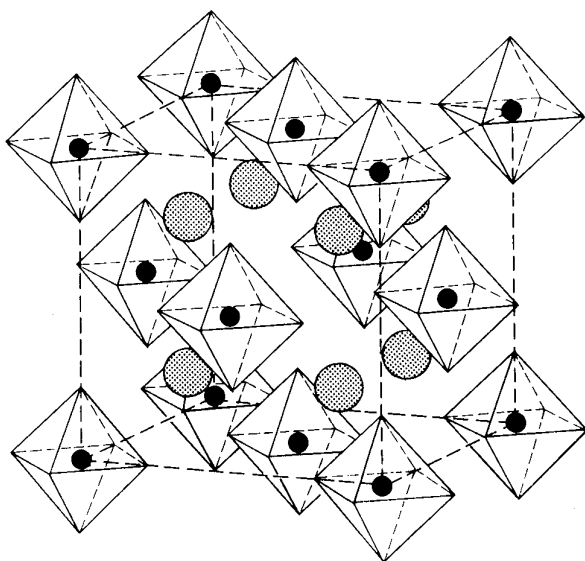


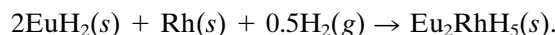
FIG. 2. The crystal structure of K_2PtCl_6 .

TABLE 2
Intensity Data (%)

<i>hkl</i>	[SrEu]IrH ₅		[SrEu]RhH ₅		[CaEu]IrH ₅	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
111	42	44	13	22	54	58
200			8	17		
220	100	100	100	100	100	100
311	30	25	14	12	35	32
222			5	6		
400	18	19	18	19	16	18
331	11	11	6	5	14	14
420			4	8		
422	41	37	40	37	35	36
511/333	8	8	4	4	8	10
440	7	12	13	12	10	11
531	7	8	3	4	9	10
620	10	16	16	16	12	16
533	5	3				
444	3	4	5	4		
711/551	3	5				
642	16	22	19	22	12	23
731/553	4	7	4	3		
<i>R</i>	0.14		0.14		0.09	

Note. $R = [\sum |I_{\text{calcd}} - I_{\text{obsd}}| \sum I_{\text{obsd}}]$.

700°C in approximately 700 Torr of hydrogen according to the following equation:



As in the case of the other TMHs of rhodium, this hydride is a black polycrystalline solid. Hydrogen gas was absorbed during its formation.

It is significant to note that our procedure for preparing TMHs and QMHs involves compressing the reactant powders in the form of pellets prior to the reaction. The purpose is to maximize particle-to-particle contact for the subsequent solid-gas phase reaction. It has been our experience over the years that each successful reaction is accompanied by an expansion of the pellets. For example, in the case of the Group VIII ruthenium TMHs and QMHs the expansion of the pellets is enormous,

TABLE 3
Values of the Curie Temperature (T_c), Weiss Curie Constants (Θ), and μ_{eff} for $[\text{Sr}_{2-x}\text{Eu}_x]\text{IrH}_5$

Sample	T_c (K)	Θ (K)	μ_{eff} (BM)
Eu ₂ IrH ₅	20 ± 2	24 ± 5	7.30 ± 0.10
[Sr _{0.5} Eu _{1.5}]IrH ₅	11 ± 2	20 ± 2	7.75 ± 0.10
[Sr _{1.0} Eu _{1.0}]IrH ₅	<7 (est.)	13 ± 2	7.70 ± 0.10
[Sr _{1.5} Eu _{0.5}]IrH ₅	<5 (est.)	5 ± 2	7.55 ± 0.10

TABLE 4
X-Ray Powder Diffraction Indexing Data and Intensity Data for Eu₂RhH₅

<i>hkl</i>	<i>d</i> (Å)		Intensity (%)	
	Obsd.	Calcd.	Obsd.	Calcd.
111	4.371	4.363	21	16
200	3.781	3.779	14	27
220	2.667	2.672	100	100
311	2.282	2.279	5	9
222	2.179	2.182	10	10
400	1.889	1.889	17	19
331	1.732	1.734		
420	1.689	1.690	12	12
422	1.542	1.543	47	27
440	1.335	1.336	22	12
620	1.195	1.195	18	16
444	1.091	1.091		
642	1.010	1.010	28	23
800	0.9452	0.9446		
822	0.8912	0.8906		
<i>R</i> = 0.17				

Note. $R = [\sum |I_{\text{calcd}} - I_{\text{obsd}}| \sum I_{\text{obsd}}]$.

approximately doubling its size. For hydrides incorporating the Group IX metals, i.e., Rh or Ir, it has been observed that an expansion which although significant, is not nearly as great as the expansion for the Ru containing samples.

Eu₂RhH₅ is an exception. In this case the original pellet completely disintegrates into a fine powder. In addition, we note that in the case of the Rh-containing QMHs discussed earlier the tendency for pellet disintegration increases as the europium content of the QMH increases, i.e., as *x* approaches 2.

The X-ray powder diffraction data were indexed on the basis of a face-centered cubic Bravais lattice with $a = 7.557$ Å (ESD = 0.001 Å). The indexing data are submitted in Table 4 and good agreement is noted between observed and calculated values for the interplanar spacing.

Intensity calculations were based on the *Fm*3m (No. 225) space group with europium occupying the 8c sites, rhodium in the 4a positions, and hydrogen randomly occupying 20 of the 24e locations. These results are, also, reported in Table 4. The data were gathered and interpreted as described earlier in this paper.

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