JOURNAL OF SOLID STATE CHEMISTRY 43, 295–298 (1982)

Modification of Hydriding Properties of $LaCo_5$ by Partial Substitutions ($LaCo_{5-x}M_x$ with M = Al, Ga)*

H. OESTERREICHER AND J. ELTON

Department of Chemistry, University of California, San Diego, La Jolla, California 92093

Received January 28, 1982; in final form March 26, 1982

By partial substitution of Co in $LaCo_5$ by nontransition metals such as Al, an increase in H capacity (z) vis-a-vis $LaCo_5$ is achieved at pressures on the order of 100 atm at room temperature. Lower equilibrium pressures, P_e, have been previously observed when compounds such as $PrCo_5$ and $LaNi_5$ were partially substituted on transition metal sites by nontransition metals such as Al, Be. This fact, coupled with the existence of the high-pressure phase $LaCo_5H_z$ with $z \cong 9$, suggests that the increased z is due to a lowering of P_e of the high-pressure phase to more modest conditions in temperature and pressure. The actual $P(z)$ curves are, however, complex and reflect phenomenology often observed with pseudobinaries.

Introduction

The understanding of hydriding phenomenology in compounds between electropositive metals and transition metals was greatly stimulated by the initial findings of characteristic responses on partial substitutions of hydrogen uptake, z, and equilibrium pressures, P_e. A lowering of P_e and z was first found to occur after partial substitution of the transition metal by other transition metals, e.g., $LaNi_{5-x}M_x$, M = Cr, Fe, Co (*1*). Similar effects were first observed (*2, 3*) on partial substitution by nontransition metals on systems such as $PrCo_{5-x}Al_x$ or $LaNi_4Be$. These studies triggered a considerable subsequent effort at design of hydrogen storage materials with special properties. Of particular interest in this connection are studies on $LaNi_{5-x}Al_x$ (*4, 5*) (for more detailed references see a recent review of hydride phenomenology, Ref. (*6*)).

In this paper we continue our studies on the effects of partial nontransition metal substitutions in rare earth transition metal compounds. In particular the principle of lowering values of P_e through partial substitution is tested by examining the hydriding behavior of $LaCo_{4.4}Al_{0.6}$ and $LaCo_{4.4}Ga_{0.6}$, where a crucial difference can be anticipated compared with, say, $LaNi_{5-x}Al_x$. This has to do with the existence of a high-pressure hydride of $LaCo_5$. Besides hydride phases with z = 3.4 (β) and 4.4 (γ) at 25°C (*7*), a high-pressure phase $LaCo_5H_9$ (δ) (P_e = 1300 atm at 25°C) also exists (*8*). We therefore expected that z and P_e for the γ phase (z = 4.4) would decrease with increasing x. However, a similar trend should hold for the phase with z = 9. This should bring P_e of this higher hydride into an experimentally more accessible H_2 pressure

---

* Work supported in part by Department of Energy, Division of Basic Energy Sciences.

0022-4596/82/090295-04$02.00/0

range. This combination of effects should result in a range of composition (x) characterized by an overall increase of z at moderate pressures compared to the parent material.

Experimental

Intermetallic compounds were prepared by induction melting on water-cooled Cu boats under Ar. The components were of 99.9% purity or better. Materials were subsequently annealed for several days at 900°C under 600 mm Ar. X-Ray diffraction was used to verify the structure of matrix and hydride phases in question.

Hydride composition was determined by pressure monitoring in known volume systems. Details of these procedures have been given previously (*9*). All samples (~0.5 g) were hydrided in an apparatus utilizing calibrated volumes (~25 cm^3 total) of known temperature. The sample chamber (~4 cm^3) was contained in a constant-temperature oil bath and the sample temperature was monitored directly by a thermocouple which was in contact with a small copper holder containing the sample. Hydriding was achieved at room temperature by exposure of the materials to ~50 atm H_2. In some cases an initial activation of 400K under vacuum was required.

Results

Structural properties of the compounds $LaCo_5$, $LaCo_{4.4}Al_{0.6}$, and $LaCo_{4.4}Ga_{0.6}$ are presented in Table I. All three materials were homogeneous of $CaCu_5$ type as indicated by X-ray characterization.

All materials in the present study absorb hydrogen around ambient conditions. $LaCo_{4.4}M_{0.6}$ materials (M = Al, Ga) take up larger amounts of H_2 compared to $LaCo_5$ when measured at a pressure of ~100 atm near room temperature. Under such conditions we obtained $LaCo_{4.4}Al_{0.6}H_{5.8}$ and $LaCo_{4.4}Ga_{0.6}H_{5.0}$ as compared to $LaCo_5H_{4.7}$ for the binary hydride. Pressure–composition isotherms, $P(z)$ and $LaCo_5$ and $LaCo_{4.4}M_{0.6}$ (M = Al, Ga), are shown in Figs. 1 to 3. A sloping $P(z)$ is characteristic for the pseudobinary compounds. Partial Al and Ga substitution results in a pronounced decrease of equilibrium pressure for values of z less than 3.0.

TABLE I

LATTICE PARAMETERS OF $LaCo_5$, $LaCo_{4.4}Al_{0.6}$, AND $LaCo_{4.4}Ga_{0.6}$

Compound	a_0	c_0	c_0/a_0
$LaCo_5$	5.09	3.96	0.778
$LaCo_{4.4}Al_{0.6}$	5.13	4.01	0.782
$LaCo_{4.4}Ga_{0.6}$	5.12	3.99	0.779

Discussion

The large homogeneous regions in $LaCo_{5-x}M_x$ corroborate the crystal chemical

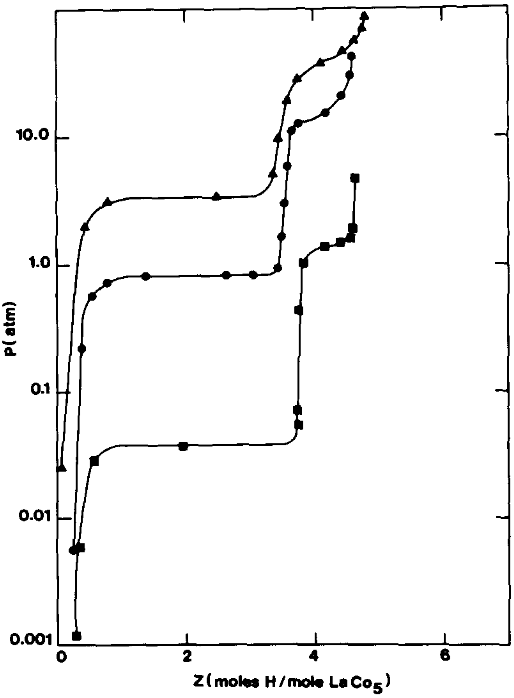

FIG. 1. Pressure–composition isotherms for $LaCo_5H_z$ at various temperatures. ■, 22°C; ●, 81°C; ▲, 116°C.

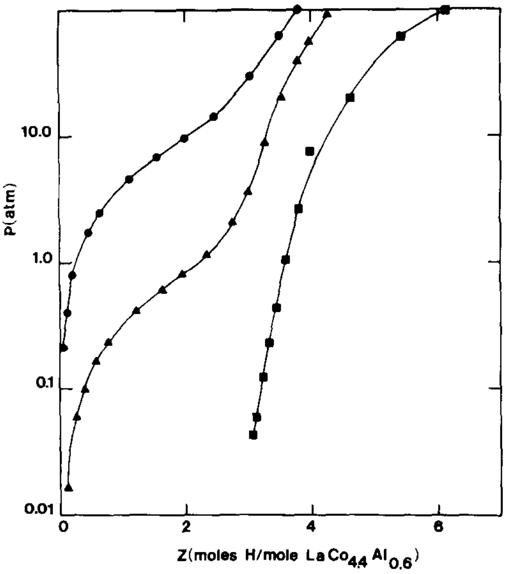

FIG. 2. Pressure-composition isotherms for $LaCo_{4.4}Al_{0.6}H_z$ at various temperatures. ■, 21°C; ▲, 117°C; ●, 215°C.

similarity of the transition metals and the IIIa elements in question. However, in the process of partial substitution considerable changes are incurred in the hydriding properties. In particular, partial Al substitution for Co in $LaCo_5$ results in increased amounts of H absorption near ambient temperatures and moderate H_2 pressures. Also a lowering of the equilibrium pressure of the lower hydride (β) of $LaCo_5$($LaCo_5H_{3.4}$) appears to be indicated. These phenomena can be understood as a result of the increased potential of attraction of H in some of the new local environments.

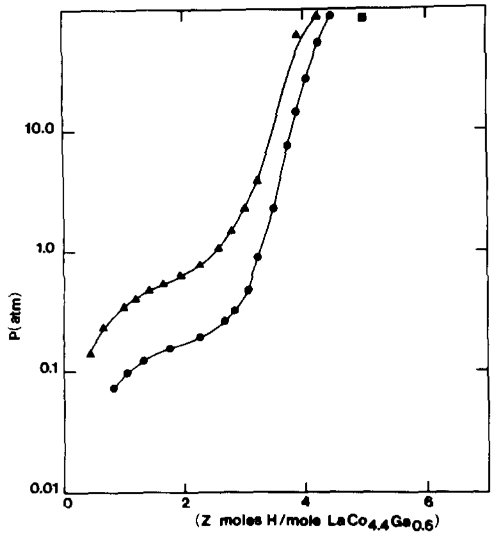

FIG. 3. Pressure-composition isotherms for $LaCo_{4.4}Ga_{0.6}H_z$ at various temperatures. ■, 23°C; ●, 77°C; ▲, 107°C.

In this connection it is interesting to note that $LaNi_{5-x}Al_x$ and $LaCo_{5-x}Al_x$ are different with respect to their behavior concerning the amount of H absorption. This indicates that there is no comparable high-pressure phase $LaNi_5H_9$ to be expected in the pressure range up to about 1000 atm—a fact corroborated by experiment (*10*). It is the lowering of the P_e of this high-pressure phase which causes the increased H absorption.

The smearing of $P(z)$ curves of the pseudobinaries compared to the well-developed plateaus characteristic of the binaries is presumably due to two different effects. The disordered substitution on crystallographic sites results in local variations of potentials of attraction for hydrogen. This effect, coupled with the expected H–H interactions being of shorter range, takes its influence on the phase transition by a lowering of the critical temperature. In addition, sample inhomogeneities on a macroscopic level may be contributing to this sloping behavior despite the relatively sharp X rays obtained on these samples.

This study therefore indicates, quite generally, new opportunities for the design of materials with special properties. Intermetallic phases in general can be assumed to harbor a number of high-pressure hydride phases. Some of these may have sufficiently "low" plateau pressures to be successfully drawn, by suitable multicomponent design, into the pressure range of conventionally available experimental facilities. In this way novel hydrogen storage materials may be arrived at by special material design.

References

1. H. Van Mal, K. H. J. Buschow, and A. R. Miedema, *J. Less-Common Met.* **35,** 65 (1974).
2. J. Clinton, H. Bittner, and H. Oesterreicher, *J. Less-Common Met.* **41,** 187 (1975).
3. H. Oesterreicher, J. Clinton, and H. Bittner, *Mater. Res. Bull.* **11,** 1241 (1976).
4. J. C. Achard, A. Percheron-Guégan, H. Diaz, F. Briancourt, and F. Demay, *in* "Proceedings International Conference on Hydrogen in Metals, Paris," Pergamon, London (1977).
5. M. G. Mendelsohn, D. M. Gruen, and A. E. Dwight, *Nature (London)* **45,** 269 (1977).
6. H. Oesterreicher, *Appl. Phys.* **24,** 169 (1981).
7. F. A. Kujpers, *J. Less-Common Met.* **27,** 27 (1972).
8. S. A. Steward, J. F. Lakner, and F. Uribe, *Advan. Chem.* **163,** 284 (1977); and J. F. Lakner, S. A. Steward, and F. Uribe, Lawrence Livermore National Laboratory, Report UCRL-52039 (1976).
9. J. A. Elton, Thesis, University of California, San Diego, La Jolla, California, Chapter II, 1981.
10. J. F. Lakner, F. S. Uribe, and S. A. Steward, *J. Less-Common Met.* **72,** 87 (1980).