

X-RAY PHOTOELECTRON SPECTROSCOPIC, ELECTRICAL AND MAGNETIC STUDIES ON Mg_2NiH_4

P. SELVAM*, B. VISWANATHAN and V. SRINIVASAN

Department of Chemistry, Indian Institute of Technology, Madras, 600 036 (India)

(First received 28 January 1988; in final form 28 March 1988)

ABSTRACT

X-ray photoelectron and X-ray induced Auger spectroscopic (XPS and XAES) investigations show that, in Mg_2NiH_4 , both Mg and Ni are in the metallic state. Support for this observation has been obtained from thermopower and magnetic measurements.

INTRODUCTION

In recent years, a large number of experimental and theoretical investigations have been devoted to the study of intermetallic hydrides, particularly Mg_2NiH_4 , which has potential for technological applications. The physical properties, viz., structural, electrical, thermal, magnetic, etc., of the hydride phase are totally different from those of the virgin alloy and discrepancies often exist in the published data [1–6]. Hence, in the present study, spectral, electrical and magnetic properties were measured for Mg_2NiH_4 along with Mg_2Ni in order to achieve a better understanding of their behaviour, especially for Mg_2NiH_4 .

EXPERIMENTAL

The preparation and characterization of the alloy and the hydride have been described elsewhere [6, 7]. The XPS and XAES measurements were carried out in an ESCALAB Mark II spectrometer (VG Scientific Ltd, U.k.) with Mg $K\alpha$ radiation with 50 eV pass energy. The working pressure in the analysing chamber was maintained below 10^{-8} torr and all measurements were carried out at room temperature. The thermopower measurements were carried out in a home-made apparatus while magnetic measurements were made on a vibrating sample magnetometer.

RESULTS AND DISCUSSION

Figure 1 shows typical Mg $2p$ XP spectra obtained for Mg_2Ni under different experimental conditions, viz., air exposed (passivated) and sputtered (clean) as

* Present Address: Laboratoire de Cristallographie aux Rayons X, Faculte des Sciences, Universite de Geneva, 24 Quai Ernest-ansermet, CH-1211 Geneva 4, Switzerland.

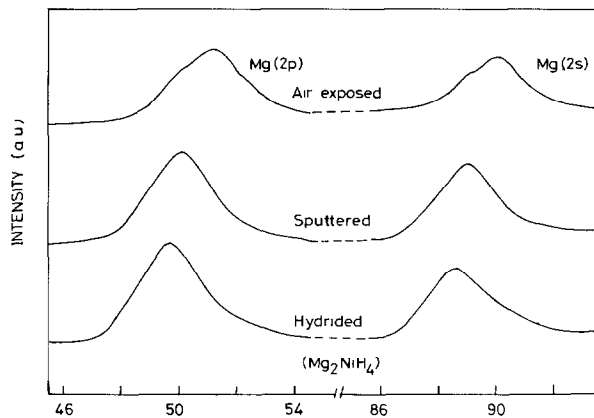


Fig. 1. XP spectra of Mg_2Ni .

well as for the Mg_2NiH_4 sample. These results indicate that the Mg in Mg_2NiH_4 is in the metallic state. The shift in the peak (about 1.5 eV) in air exposed Mg_2Ni reveals that Mg is oxidised; correspondingly a chemically shifted peak appears at the high binding energy (BE) side [7, 8]. In Mg_2NiH_4 , the peak appears in the metallic region (or even slightly shifted to the low BE side). Moreover, the position of the peak of the Ni $2p$ level reveals that it is mainly in the metallic state, thus suggesting a metallic behaviour of Mg_2NiH_4 (Fig. 2), similar to that observed for Ni in sputtered Mg_2Ni (see Fig. 2). However, the air exposed Mg_2Ni alloy shows two peaks ($2p_{3/2}$ region), clearly separated from the metal core levels, indicative of the presence of Ni as NiO and Ni(OH) $_2$. The presence

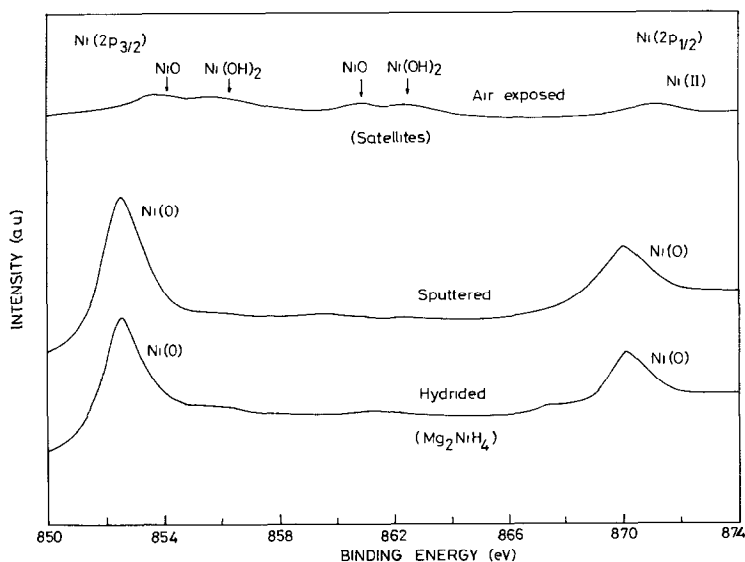


Fig. 2. XP spectra of Mg_2Ni .

of these are further evidenced by their characteristic shake-up features appearing about 6.0–7.0 eV away from the respective main peaks [7, 8].

The Ni *LMM* Auger transition (Fig. 3) also gives pertinent information on the nature of the species present on the samples. For example, the sputtered and hydride (Mg_2NiH_4) alloy shows sharp peaks, typical of metallic Ni. Moreover, the XPS doublet $2p_{1/2}$, $2p_{3/2}$ separation energy in sputtered and hydrided samples show almost the same values (as may be seen from Fig. 2) suggesting the presence of Ni in Mg_2NiH_4 in the metallic state. However, the XAES Ni *LMM* transition for the air exposed sample (Fig. 3) shows a broad spectrum due to the presence of NiO and $\text{Ni}(\text{OH})_2$ on the surface in conformity with the results deduced from the XP spectra of $\text{Ni}2p_{3/2}$ region. Argon ion bombardment results in a gradual decrease in the oxide contamination layers, leading to a sharpening of the peak characteristic of metallic Ni. Thus, XPS and XAES results on Mg_2NiH_4 suggest that Ni is present in the zero valent state. If it had an ionic character $\text{Mg}_2^{\delta+}\text{NiH}_4^{\delta-}$ [9] or if it were considered to be completely ionic with Mg cations (Mg^{2+}) and tetravalent (NiH_4^{4-}) complex

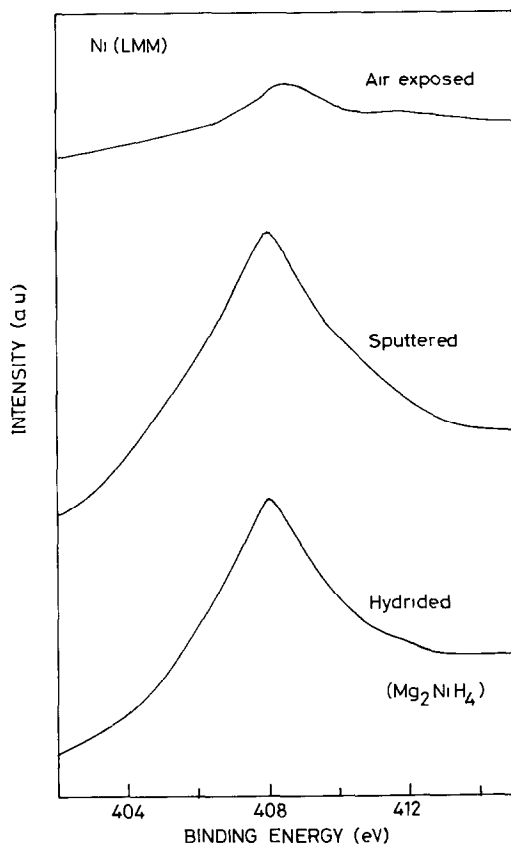


Fig. 3. XAES spectra of Mg_2Ni .

anions (the actual charges are of course different) [10] the binding energies of the core levels of both Mg and Ni should show shifts in opposite directions compared to the zero valent states. The present study shows however, a metallic behaviour for both the elements, Mg and Ni.

In order to confirm the metallic behaviour of Mg_2NiH_4 , thermoelectric power (Seebeck coefficient, α) measurements were carried out over the temperature range 100–300 K (Fig. 4). These results indicate that electrons are the major carriers. Typical values of α for Mg_2NiH_4 are in the range $3\text{--}6\ \mu\text{VK}^{-1}$. The measurements carried out on the parent alloy, Mg_2Ni indicate that the α -value is about $1\ \mu\text{VK}^{-1}$ at 300 K. The α -value of Mg_2NiH_4 is characteristic of materials lying in between semimetals and narrow band semiconductors, but is higher than expected for the pure metal. The α - T measurements clearly indicate an increase in the thermopower value with hydrogenation. However, the data indicate a metal-like behaviour with decreasing thermopower value as the temperature is lowered (Fig. 4). Since the α - T plot shows a discontinuity at about 150 K, one can expect some ordering in the structure, possibly magnetic. The magnetic behaviour of this compound as a function of temperature is worth investigating and work is in progress. The room temperature magnetic measurements of polycrystalline Mg_2Ni indicate paramagnetic nature with a susceptibility of $0.3 \times 10^{-6}\ \text{emu g}^{-1}$. The value is higher for the hydrided sample (Mg_2NiH_4 , $0.2 \times 10^{-5}\ \text{emu g}^{-1}$) and this is consistent with the literature data [2].

The resistivity measurements performed at room temperature showed a value of $3.5 \times 10^{-2}\ \Omega^{-1}\text{cm}^{-1}$. This rather high conductivity is in agreement with the reported values [4, 5]. The absorption spectrum also supports this view, in which it shows two absorption maxima, corresponding to the band gaps at 2.4 eV and at 2.0 eV (Fig. 5). This may mean that Mg_2NiH_4 has two band gaps one direct and the other indirect. In addition, two other small absorption maxima with large band gaps ($> 2.5\ \text{eV}$) also appear.

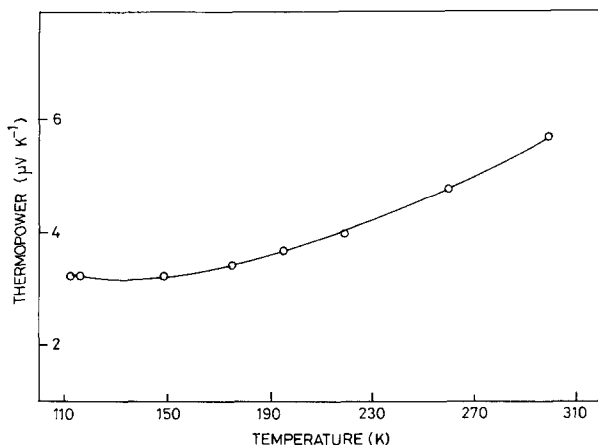


Fig. 4. Thermopower versus temperature plot for Mg_2NiH_4 .

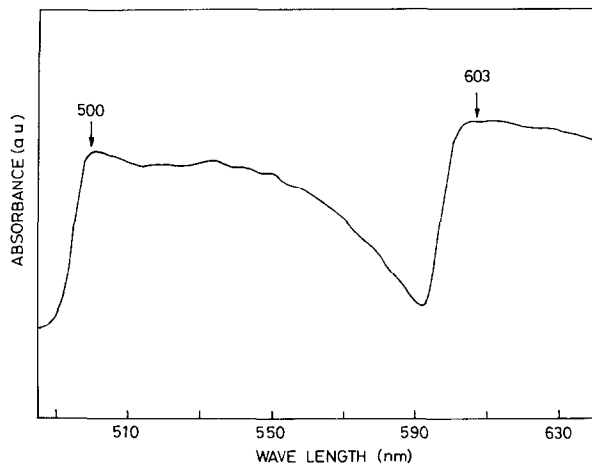


Fig. 5. Optical spectrum of Mg_2NiH_4 .

In the present investigation, Mg_2NiH_4 was found to possess near metallic/semiconducting properties. However, the question as to whether Mg_2NiH_4 is a real metal or a semiconductor has yet to be answered. The XPS, electrical and magnetic studies reported in this paper favour a metallic state. Further investigations are required to obtain more details on these properties. It is also to be noted that the knowledge of H atom distribution in Mg_2NiH_4 is essential for theoretical energy band calculations, which in turn give better insight into the chemistry and physics involved in this compound.

ACKNOWLEDGEMENT

The assistance and helpful discussions with Mr. S. Natarajan of the Material Science Research Centre for the electrical measurements are gratefully acknowledged. The authors wish to thank the Regional Sophisticated Instrumentation Centre for the XPS measurements.

REFERENCES

- 1 F. Stucki and L. Schlappbach, *J. Less-common Met.*, 74 (1980) 143.
- 2 L. Schlappbach, F. Stucki, A. Seiler and H.C. Siegmann, *J. Magn. Mater.*, 15-18 (1980) 1271.
- 3 M. Gupta, E. Melin and L. Schlappbach, *J. Less-Common Met.*, 103 (1984) 389.
- 4 D. Noreus, K. Jansson and M. Nygren, *Z. Phys. Chem. N.F.*, 146 (1985) 191.
- 5 D. Garva, G. Kimmel, Y. Gefen and M.H. Mintz, *J. Appl. Phys.*, 57 (1985) 4548.
- 6 P. Selvam, B. Viswanathan, C.S. Swamy and V. Srinivasan, *Bull. Mater. Sci.*, 9 (1987) 21; *Int. J. Hydrogen Energy*, 13 (1988) 87; *Thermochim. Acta*, 125 (1988) 1.
- 7 P. Selvam, Ph.D. Thesis, Indian Institute of Technology, Madras (1987).
- 8 P. Selvam, B. Viswanathan and V. Srinivasan, *Int. J. Hydrogen Energy*, submitted.
- 9 J. Genossar and P.S. Rudman, *J. Phys. Chem. Solids*, 42 (1981) 611.
- 10 K. Yvon, *J. Less-Common Met.*, 103 (1984) 53.