

MÖSSBAUER STUDY OF ^{151}Eu IN HYDROGEN - LOADED PALLADIUM

M. MEYER and J.M. FRIEDT

Laboratoire de Chimie Nucléaire

Centre de Recherches Nucléaires associé à l'Université Louis Pasteur

B.P. 20 67037 - STRASBOURG-Cedex (France)

L. IANNARELLA and J. DANON

Centro Brasileiro de Pesquisas Físicas

RIO DE JANEIRO (Brésil)

ABSTRACT

The decrease of the ^{151}Eu isomer shift on hydrogenation of a dilute EuPd (2.5 at % Eu) alloy is discussed in terms of the volume effect on the charge density at the nucleus.

INTRODUCTION

A number of recent works were concerned with the changes of electronic distribution on diluting a Mössbauer element in palladium and on further hydrogenation of the alloy [1, 2, 3]. Hereby a substantial modification of the electron density in the conduction band of palladium metal ($4d^{9.64}5s^{0.36}$ original configuration) has been observed. Metallic palladium easily absorbs large quantities of hydrogen (up to about 70 at %). At 300°K, the Pd-H system exhibits two phases (α and β); a strong lattice expansion is associated with the hydrogen absorption [4].

The Mössbauer study of a dilute impurity in Pd on hydrogenation is basically expected to reveal changes of the conduction band population due to electron transfers from or towards the hydrogen atom and to an apparent pressure effect associated with the expansion of the host lattice [1, 2, 3].

The 21 keV resonance of ^{151}Eu is particularly suited for electron density studies because of the high sensitivity of the isomer shift (IS) due to the large change in the nuclear charge radius between the excited and ground states : $\Delta\langle r^2 \rangle = 19,2 \times 10^{-3} \text{fm}^2$ [5]. We report here the electronic changes on hydrogenation of a dilute EuPd alloy (2.5 at % Eu) from ^{151}Eu IS measurements.

EXPERIMENTAL AND RESULTS

The EuPd alloy was obtained by melting the metals in an induction furnace under purified argon atmosphere. The alloy was checked by X ray diffraction measurements, yielding a value of the fcc lattice constant $a_0 = 3.920 \text{ \AA} \pm 0.002 \text{ \AA}$, in agreement with ref.6. The hydrogenation was carried out electrolytically in 0.1N H_2SO_4 with a current density of 50 mA/cm^2 and the H content was determined by weighing.

The Mössbauer spectrum of EuPd measured at 4.2°K versus a Sm_2O_3 source at the same temperature reveals a single line with an isomer shift of $3.42 \pm 0.02 \text{ mm/s}$ [6]. On hydrogenation of the alloy, the spectrum still exhibits a single resonance line progressively shifted towards lower velocities, down to $3.06 \pm 0.02 \text{ mm/s}$

in the saturated material (figure 1). The resonance area, which in the described experiments is proportional to the Lamb Mössbauer factor of the absorber decreases on hydrogenation. Typical values for the resonance effect at 77°K (non corrected for background) before and after hydrogenation are 8.35 % and 7.36 % respectively.

The X-ray diffraction studies of the alloy containing 26 and 40 at % H reveal the coexistence of both α and β phases of Pd-H whereas the pure α phase is observed for 11 at % H. At H concentration higher than 40 at % the β phase pattern appears alone with broadened diffraction lines [4]. The lattice constant in the saturated alloy is 4.04 ± 0.01 Å. Thus, for the intermediate H concentrations, the Mössbauer spectra should comprise two unresolved lines, corresponding to the two phases in variable proportions. Indeed a slight broadening of the resonance line (from 2.72 ± 0.03 to 2.81 ± 0.03 mm/s) is observed on hydrogen loading and computer simulation allowed to check that this behaviour is consistent with the assumed situation.

DISCUSSION

The IS of ^{151}Eu in EuPd is characteristic of the trivalent configuration ($4f^6$) of the rare earth impurity, associated to a rather high population of the 6s conduction band [6]. The evolution of the IS after hydrogen loading shows that the matrix is affected as a whole, which contrasts with the formation of an hydride as observed in metallic europium [9].

The decrease of electron density at the Eu nucleus, reflected by the decrease of IS after H loading, can basically be attributed to a volume effect alone.

The change of total electron density associated to the volume effect is indeed known from studies of the pressure dependence of the IS of europium systems and the coefficient $\Delta\rho/\Delta\ln v$ has been deduced to be between -19 and -14 a_0^{-3} [7]. The relative volume change in the hydrogen saturated EuPd alloy is $\frac{\Delta v}{v} = 0.09$. With these data one calculates a decrease of $-0.46 \pm 0.06 \text{ mm/s}$ in isomer shift accompanying the volume change. The calculated value is in reasonable agreement with the experimental result. The interpretation is also supported by the observed decrease of the f factor. The conduction electron contribution to the IS has been recently evaluated from an energy band calculation for bcc metallic Eu. The $6s$ electron density of the metal yields a volume coefficient of $(\Delta\rho/\Delta\ln v) = -16 \text{ a}_0^{-3}$ [8]. It is concluded that the change in $\rho(0)$ associated with the hydrogenation of the EuPd alloy arises essentially from a uniform decompression of the $6s$ conduction electrons.

The experimental result might of course also be accounted for assuming a trapping of the $6s$ Eu electrons by the hydrogen atoms as it occurs in the pure metal where the hydrogenation leads to the formation of the divalent hydride EuH_2 [9]. There is however no evidence for such a mechanism from the present investigation.

ACKNOWLEDGMENTS

We are most grateful to Dr. G. Jehanno for his help in preparing the alloy and to F. Wagner and U. Wagner for helpful discussions.

REFERENCES

1. W.C. PHILLIPS and C.W. KIMBALL, Phys. Rev. 165, 401 (1968)
A.E. JECH and C.R. ABELEDO, J. Phys. Chem. Sol. 28, 1371 (1967)
2. L. IANNARELLA, F.E. WAGNER, U. WAGNER and J. DANON
J. Physique C6, 517 (1974)
3. J.S. CARLOW and R.E. MEADS, J. Phys. F2, 982 (1972)
4. F.A. LEWIS, The Palladium Hydrogen System,
Acad. Press, New York (1967)
5. G.M. KALVIUS and G.K. SHENOY, Atomic Data and Nuclear Data
Tables 14, 639 (1974)
6. I.R. HARRIS and G. LONGWORTH, J. of Less Common Metals, 23,
281 (1971)
7. G.M. KALVIUS, U.F. KLEIN and G. WORTMANN, J. Physique C6, 139
(1974)
8. S. KOBAYASI, M. FUKUCHI and S. NAGAI, Sol. State Comm. 13,
727 (1973)
9. A. MUSTACHI, J. Phys. Chem. Sol. 35, 1447 (1974)

