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MÖSSBAUER STUDY OF TRANSITION METAL IMPURITIES IN HYDROGEN-LOADED PALLADIUM

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Résumé. — On a étudié l'influence du chargement d'une matrice de palladium avec de l'hydrogène sur les déplacements isomériques d'impuretés de ^{197}Au , ^{195}Pt , ^{193}Ir et ^{99}Ru . Dans tous ces systèmes on a trouvé que la densité d'électrons aux noyaux des impuretés Mössbauer décroît comme conséquence de l'hydrogénisation. Le décroissement est comparable à la différence des densités d'électrons observée dans des matrices de Pd et de Ag.

Abstract. — The influence of hydrogen-loading of a palladium matrix on the isomer shifts for impurities of ^{197}Au , ^{195}Pt , ^{193}Ir and ^{99}Ru has been studied. In all these systems the electron density at the nuclei of the Mössbauer impurity has been found to decrease on hydrogenation. The decrease is comparable to the electron density difference observed between Pd and Ag matrices.

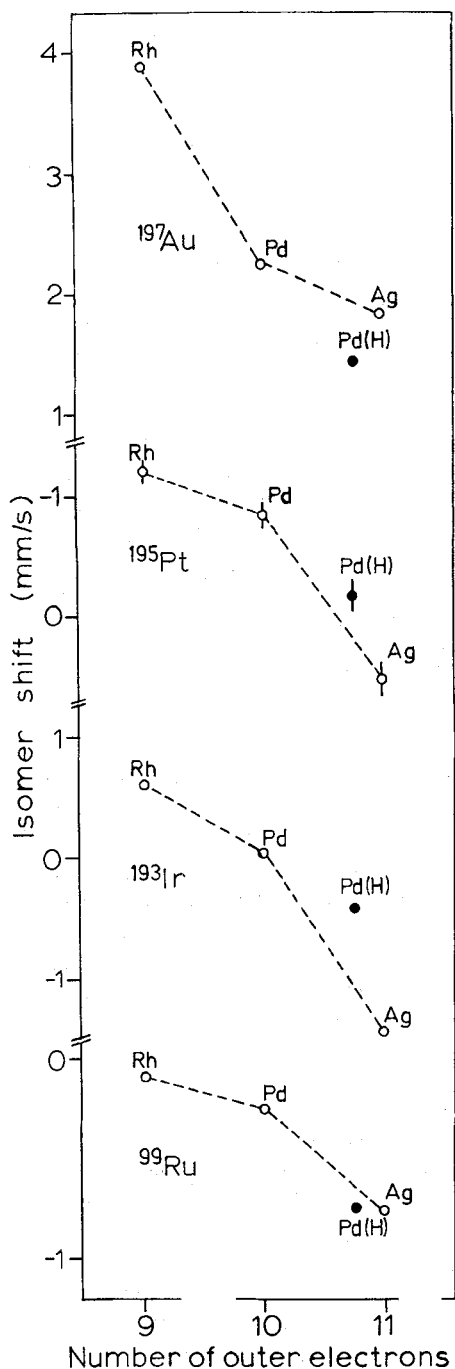
The influence of hydrogen loading of the host matrix on the Mössbauer isomer shifts of transition metal impurities has to date mainly been studied with the 14.4 keV resonance of ^{57}Fe [1-4]. These experiments have shown that in Ni, Nb, and Pd matrices the electron density at the ^{57}Fe nuclei decreases on hydrogenation. Recently [5] the same behaviour has been observed for the 6.2 keV resonance of ^{181}Ta in hydrogen-loaded tantalum metal. In the present work we have used the Mössbauer resonances in ^{197}Au (77 keV), ^{195}Pt (99 keV), ^{193}Ir (73 keV), and ^{99}Ru (90 keV) to study the effect of hydrogen loading on the electron density at the nuclei of these isotopes introduced as dilute impurities into a palladium matrix.

For the measurements on ^{197}Au a source of ^{197}Pt in Pt metal and an absorber consisting of a $\text{Au}_{0.01}\text{Pd}_{0.99}$ alloy were used. In the other cases absorbers of pure Pt, Ir, and Ru metal were used together with sources of the compositions $\text{Pt}_{0.004}\text{Pd}_{0.996}$, $\text{Os}_{0.02}\text{Pd}_{0.98}$, and $\text{Ru}_{0.005}\text{Pd}_{0.995}$ containing the $^{195\text{m}}\text{Pt}$, ^{193}Os , and ^{99}Rh activities that populate the respective Mössbauer levels. The Pd alloys were arc-melted and rolled to thin foils. These were loaded with hydrogen electrolytically in 0.1 n H_2SO_4 for at least one day to reach saturation. The hydrogen content was monitored gravimetrically with an accuracy of about 10 percent. The composition of the loaded foils was found to be near $\text{PdH}_{0.8}$ in all cases. After being taken from the electrolytic bath, the samples were rapidly cooled to liquid nitrogen temperature as a precaution against outgassing. The Mössbauer measurements were performed at liquid helium temperature. The isomer shift results obtained before and after hydrogenation

are summarized in figure 1. The linewidths were not sensitive to hydrogen loading except for the case of ^{193}Ir , where an increase of about 10 percent was observed for the sample containing hydrogen.

For comparison figure 1 also gives the isomer shifts observed [6-8] for the individual Mössbauer resonances in pure Rh and Ag hosts. The isomer shift data are plotted versus the number of electrons in the conduction band of the host. For $\text{PdH}_{0.8}$ this number will be 10.8, if each hydrogen atom donates one electron into the conduction band of Pd as is assumed by the protonic model of metal-hydrogen systems. One finds that, for all four cases, the electron density at the Mössbauer nuclei decreases with an increasing number of outer electrons. This tendency exists in the pure Rh, Pd, and Ag hosts as well as in Pd on hydrogen loading. One should note that ^{57}Fe also shows this behaviour [2]. The amount by which the electron density changes between Pd and $\text{PdH}_{0.8}$ is of the same order of magnitude as the electron density difference found between Pd and Ag as host matrices, but there are marked differences, for instance, between ^{197}Au and ^{193}Ir , the former having an even lower and the latter a considerably higher electron density in $\text{PdH}_{0.8}$ than in the Ag matrix.

Naively, one may distinguish between two mechanisms contributing to the electron density difference between pure and hydrogen-loaded Pd, namely the volume expansion and the filling of the host conduction band with electrons donated by the hydrogen. Volume expansion will lower the electron density, but lacking information on the magnitude of the volume coefficient of the isomer shifts for the studied systems, we cannot estimate the magnitude of the volume effect. The fact



that, in all cases studied to date, the dissolution of hydrogen in the Pd lattice leads to a decrease of the electron density indicates, however, that either the volume effect dominates in all these cases, or that the filling of the host conduction band also results in a decrease of the electron density at the impurity nuclei.

For a Pd host, in particular, the latter behaviour seems strange since, with pure Pd having only about 0.36 d-holes in the band [9], hydrogen loading to the composition $\text{PdH}_{0.8}$ should result in a considerable increase in s conduction electrons. This one might expect to cause an increase rather than a decrease of the electron density at the impurity nuclei. To explain the actual behaviour, one may assume that the filling of the s states in the band does not increase the s, but rather the d electron population at the impurity site [2]. Alternatively, however, it seems possible that the dominating effect on the electron density at the impurity nucleus comes from the core electrons of the impurity, whose density at the nucleus may be changed by overlap and orthogonalization effects. An experimental indication for such a mechanism to be of importance for the explanation of isomer shifts in transition metal alloys has recently also been found from conversion electron studies of the 4s electron density at iron nuclei in various transition metal hosts [10].

FIG. 1. — Isomer shift results for impurities of ^{197}Au , ^{195}Pt , ^{193}Ir , and ^{99}Ru in hydrogen-loaded Pd matrices. All shifts are given relative to the respective metals. Their signs are such as would be observed in absorbers of the individual alloys. The isomer shift scales have been chosen in such a way that the electron density at the Mössbauer nuclei increases from the bottom to the top of each plot. The full dots are the results for $\text{PdH}_{0.8}$ hosts, the open ones those for non-hydrogenated Pd, Rh, and Ag hosts. Except for ^{195}Pt , the experimental errors are smaller than the size of the dots.

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