Chapter-IX
Introductory Remarks

The study of hydrogenated metals by X-ray spectroscopic methods can be divided into two parts:

(1) By x-ray absorption spectra
(2) By x-ray fluorescence spectra

The x-ray absorption in PdH was studied first by Hanawalt (1930) who recorded the L_{111} edge of Pd before and after hydrogen diffusion. The main result of this investigation was the changes in the extended structure today known as EXAFS. Nothing beyond the lattice expansion of the metal was revealed in these studies. Lewis (1960) recorded the K-edge of Ni subjected to hydrogen diffusion by pressure. The results showed a slight change in the relative intensities of the log Io/I vs. 2θ curve. The small perturbations were attributed to the atomlike energy states in the system.

In 1959 were published the first interesting results of Baranowski school who found that if hydrogen is diffused electrolytically in presence of thiourea, large amount of hydrogen gets diffused into the system. The resulting nickel lattice gets expanded according to the x-ray diffraction results of Janko (1960). Paessler and Schmid (1966) recorded the K edge of Ni before and after H-diffusion. Their results are shown in Fig. 9.1. The EXAFS shows not only lattice expander-
**Figure 9.1**

K absorption edge of the Ni before and after hydrogenation. Faessler and Schmidt (1966)
sion but also a change in the shape of the K-edge. Before diffusion the edge has a small link in its slope. This is generally referred to as K\textsubscript{1} K\textsubscript{2} structures by most of the workers in x-ray spectroscopy (e.g. Cauchois).

These features are interpreted as IS→3d and IS→4p transitions. Normally IS→3d is a forbidden transition in an atom but in the metallic state the d-character is no longer preserved in its pure form and this transition is weekly allowed. After hydrogen, the d-band gets filled and the IS→3d transition is no longer seen. The edge has a smooth running shape. As the figure shows, Δev of IS→4p from IS→3d is 11.5 ev. In these experiments the hydrogenated Ni-foil was replaced after every 20 minures time by a freshly loaded sample. During this time a part of the hydrogen escaped out. To have a check on the results of Faessler and Schmidt an experiment was carried out in the laboratory in which a nickel foil loaded continuously with hydrogen was subjected to an EXAFS recording. However, since a sealed x-ray tube was used the WL \textsubscript{112} lines emitted by the tungsten metal deposited on the anticathode interfered with the K-edge of Ni masking the edge and the rear structure. Only the EXAFS could be seen. We shall describe these results in details in the next chapter.

Fukai and Kazana (1976) studied vandium diffused by hydrogen. They studied the soft x-ray L\textsubscript{3} emission band and found evidence for the H-induced states first suggested by Eastman et.al (1971).
Effect of hydrogen diffusion on the x-ray emission spectra recorded in fluorescence have been studied. VHx system by Brylov et.al (1973), CrHx by Brumen et.al (1975) and TiHx by Nemnonov et.al (1966), however, we shall confine here our discussion on Pd and Ni.

Gilberg (1971) and Hanus and Gilberg (1975) studied the LB, emission from NbHx and PdHx. In NbHx they found an additional emission showing the existence of the induced states but in PdHx they failed to see any such thing. No reason has so far been assigned to this mysterious absence. It is the opinion of the present author that Eastman et.al have stressed that the induced hydrogen states have dominantly a p-character.

No wonder, that a transition from such states to \( L_{11} \) or \( L_{111} \) level is not allowed and cannot be seen in the neighbourhood of \( L_B \) line. The question then arises as to why it is observable in NbHx?

The results for \( K\sigma_{1,3} \) emission lines of Nickel were reported earlier (Krishnan 1971). The lines in hydrogenated samples show a shift of 12 ev on the higher energy side with respect to the unhydrogenated metal. We shall attempt to interpret these results in the chapter that follows the reset one.
REFERENCES


Janko, A. (1960), Die Naturwissens Chaften, 10, 255.