X-RAY ABSORPTION NEAR EDGE STRUCTURE OF METAL HYDRIDES

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ABSTRACT

We have measured the X-ray absorption near edge structure
(XANES) at K, L_1, L_2 and L_3 edges of Ti, V, Cr, Ni, Zr, Nb,
La, Ce and Lu hydrides. The p-projected densities of empty
states for Ni and NiH have been derived from band structure
calculations which extend to 36 eV above the Fermi level. We
show that the structure in the absorption edge of Ni hydride
reflects the structure for the p-projected density of empty
states.
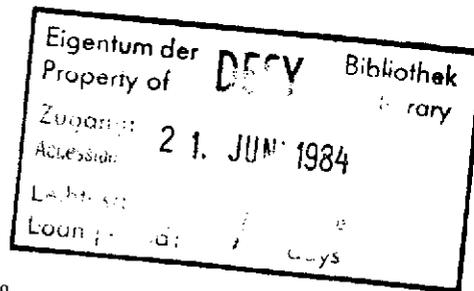
1.   Introduction

A major breakthrough in the understanding of the electronic
structure of hydrogen in metals has been achieved by the band
structure calculations of A.C. Switendick and later by many
other groups /1-7/. The basic points emerging from these calcu-
lations are the following:

1. Among the electronic host states, those most strongly affec-
ted by the dissolved hydrogen have s-character at the hydrogen
site.

2. Since the proton is a strong perturbation, electronic states
can be shifted in energy by considerable amounts (up to 10 eV).

3. The dissolution of hydrogen is favored strongly if states
which are empty in the host are shifted by hybridisation with
hydrogen wavefunctions below the Fermi level.

4. In metal-hydrogen systems with more than one hydrogen per
unit cell the H-H interaction can create new states below the
Fermi level E_F.

5. If not enough new states are created and if not enough empty
states are shifted below E_F the remaining electrons have to be
accomodated at the Fermi level.

The band structure calculations are the best basis for explaining
the various experimental results on hydrides obtained with very
different techniques: Electronic specific heat, magnetic suscep-
tibility and magnetization, nuclear magnetic resonance (see e.g.
/1/), Mössbauer effect /8/, de Haas-van Alphen effect /9-10/ and

Compton scattering /11/ have all been used to study H in metals. Techniques which probe densities of occupied and empty electronic states such as photoemission /12/ and photoabsorption are especially interesting for testing band structure calculations.

In the present paper we present X-ray absorption measurements on Ti, V, Cr, Ni, Zr, Nb, La, Ce and Lu hydrides which were used to determine p- and d-projected densities of empty states. We have performed a band structure calculation for Ni and NiH from which the density of empty p-states was deduced. We will show that the structure in the K edge of nickel hydride basically reflects the structure in the empty p-states.

2. X-ray absorption near edge structure (XANES)

Figure 1 shows the principle of the technique /13/. When the energy E of a photon exceeds the binding energy E_0 of e.g. a 1s electron in Ni then a K absorption process can occur. Due to the conservation of angular momentum transitions are only allowed (in the dipole approximation) between electronic states with $|\Delta \ell| = 1$. This means that a 1s or 2s electron can only end up in empty p-states (K and L_1 absorption). Electrons from 2p states will end up mainly in d states (L_2 and L_3 edges). The XANES spectroscopy probes the empty, projected, local electronic densities of states $D_\ell(E)$. Müller et al /14/ have shown that the X-ray absorption coefficient μ can be written as

$$\mu(E) \sim m_\ell(E) \ D_\ell(E) \qquad (1)$$

The transition matrix element $m_\ell(E)$ is weakly dependent on the energy. The structure in μ reflects basically the structure in $D_\ell(E)$. The first X-ray absorption measurements on hydrides were done with photons from X-ray tubes /15-16/. These measurements were hampered by the poor energy resolution which smears out the details in the structure of the edges and hence can lead to a wrong location of the Fermi level. With the advent of highly collimated, intense and tunable X-rays from storage rings the situation has improved considerably on the experimental side as will be shown.

3. Experimental details

The samples used in the present investigation were prepared from high purity metals by gas absorption ($TiH_{1.90\pm0.01}$, $VD_{0.72\pm0.01}$, $ZrH_{1.98\pm0.01}$, $NbH_{0.93\pm0.01}$, $LaH_{2.00\pm0.02}$, $LaH_{2.96\pm0.02}$, $CeH_{1.92\pm0.02}$, $CeH_{2.65\pm0.02}$, $LuH_{1.96\pm0.05}$, $LuH_{3.0\pm0.05}$) or by electrolysis ($CrH_{1.00\pm0.01}$ and $NiH_{0.85\pm0.01}$). Ni foils of 5 μm thickness were charged at room temperature in 1 n sulfuric acid (50 mA/cm^2, Pt anode) for 24 hours. A 5 μm thick film of chromium hydride was deposited on 2.5 μm Cu foils in a solution of CrO_3 and water according to a method described by Knödler /17/. The Ni and Cr hydrides were stored in liquid nitrogen in order to prevent the hydrogen from escaping from the samples. The hydrogen concentration in these alloys was determined by heat extraction. The lattice constants (at 25 °C) of hexagonal CrH were found by X-ray diffraction to be a = 2.719 Å and c = 4.430 Å. The hydrogen concentration in the other hydrides was determined from

the amount of absorbed gas. These hydrides were ground in an agate mortar in a glove box and stored under purified argon. Immediately before the measurements powder layers of appropriate thickness were packed between two Kapton foils. In addition to the hydrides metal foils of high purity were analysed.

All measurements were done in transmission at the beam line ROEMO at the Hamburger Synchrotronstrahlungslabor. The photon intensities were measured by ionisation chambers. For photon energies E below 10 keV a Si(111) double crystal monochromator was used with an energy resolution of 1.5 eV FWHM at 10 keV. For energies above 10 keV a Si(220) cut was used (energy resolution 1.2 eV at 10 keV). The first crystal of the monochromator was cut asymmetrically with an angle of 5° between the surface and the reflecting planes. For the second crystal this angle was zero. This allows rejection of the harmonics without loss of intensity. The amount of harmonics was continuously monitored by means of a NaI scintillation counter. The electron energy in the storage ring DORIS was 3.7 GeV. Small shifts in the beam position and beam direction are especially embarrassing in XANES studies since they can produce changes in the photon energy (at the same monochromator setting) by 0.5 eV or more. In order to distinguish this effect from real shifts in the edges e.g. between Ni and Ni hydride we have measured at the same time with the edge of Ni hydride the edge of a pure Ni between the second and a third ionisation chamber. This arrangement of three ionisation chambers in a row with two samples measured at the same time allows one to locate the absorption edges relative to one another with an accuracy of $\pm$ 0.1 eV.

4. Experimental results

The figures 2-3 show the K edges of Ti, V, Cr, Ni, Zr and Nb in the pure metals and in the hydrides listed above. The jumps at the edge have been normalized to one. The pure metals show increasing structure in the edges with decreasing atomic number Z. An especially strong peak is visible in the edge of metallic Ti. As a rule, the K edges of the hydrides have less pronounced structures. This is also true for the L_1 edges of La, Ce and Lu hydrides (figure 3,4). The L_3 edges of the rare earths and their hydrides are characterized by strong white lines which reflect the high density of empty d-states just above the Fermi level. The normalized L_2 and L_3 edges are identical. There are only minor differences in the L_1, L_2 and L_3 edges of the di- and trihydrides of the rare earths (figures 3,4).

5. Band structure calculations for Ni and NiH

We have performed band structure calculations for Ni and NiH using self-consistent potentials obtained by the local density approximation /18/ to the density functional theory. The lattice parameters used for the fcc Ni and NiH were 3.47 $\overset{\circ}{A}$ and 3.724 $\overset{\circ}{A}$, respectively. The value for the NiH was taken from our EXAFS analysis on $NiH_{0.85}$. The value for Ni is a theoretical one, determined by the self-consistent potential of Moruzzi et al /20/ which we use in our calculation. The experimental lattice parameter for Ni at 77 K is 3.514 $\overset{\circ}{A}$ /19/.

The KKR method used in the present calculation for Ni is des-
cribed in reference 20. The expansion of the wavefunctions in
spherical harmonics is truncated at $\ell = 4$. Figure 5 shows the
result of the calculation for Ni. In the case of NiH a similar
procedure to that adopted for Ni was not possible. We have con-
structed a self-consistent potential by the linear band structure
method of augmented spherical waves /5,21/. Since this linear me-
thod does not yield accurate unoccupied bands at higher energies,
the potential was brought into muffin-tin form and the bands
were calculated by the APW method (figure 5). The wavefunctions
at the symmetry points Γ, X, W, L and U = K were analysed accor-
ding to their ℓ-character at the Ni sites and at the octahedral
sites in Ni and NiH. The predominant character is marked in fi-
gure 5 on the left hand side of a symmetry point for the Ni site
and on the right hand side of a symmetry point for the octahedral
site (which is empty in Ni and occupied by hydrogen in NiH). A
comparison of the two band structures shows that the main changes
occur for those states which have s-character at the octahedral
site and these are lowered considerably in energy by the attrac-
tive potential of the hydrogen. Some states which are empty in
Ni (like L_2') are lowered below the Fermi level in the hydride.
They accomodate part of the additional electrons. The rest of
these is accomodated in the lowest free states thus moving up
the Fermi level above the d-bands. The results obtained in the
present calculation are in qualitative agreement with those by
Switendick /1/ and Gupta and Burger /5/, but ours extend to higher
energies which is of interest for the comparison with the XANES.

In order to do this comparison we have calculated the p-projected
local density of empty states at the Ni sites using the tetrahe-
dron method for the Brillouin zone integration with 6144 tetrahe-
drons for Ni and 756 tetrahedrons for NiH. The results are shown
in figure 6. Also shown in this figure is the slowly varying ma-
trix element $m_1(E)$ for NiH which differs only slighlty from that
for pure Ni. The main effect of the hydrogen is to lower the peak
positions from 3, 8, 17 and 25 eV in pure Ni to 1, 5, 12 and 19 eV
in NiH. The first three of these peaks are related to the bands
at $X_{4'}$, W_3 and $X_{5'}$, U_4, L_2, which have mainly p character at
the Ni site. The peaks at 25 eV in Ni and 19 eV in NiH are
caused by band extrema not visible in figure 5 /22/. In the
lower part of figure 6b we show the measured K-absorption
edge for $NiH_{0.85}$ and the calculated product $m_\ell(E) \cdot D_\ell(E)$ for
NiH which has been convoluted with a Lorentzian. The width of
the Lorentzian is energy dependent. It varies between 2.6 eV at
E_o and 6.2 eV at 40 eV above E_o and takes into account the core
hole lifetime, the final state lifetime /14/ and the experimen-
tal resolution (quoted above). The theoretical energy scale has
been expanded by 5 %. The fair agreement between theory and ex-
periment shows that the structure in the XANES is mainly due to
the structure in $D_\ell(E)$. The need for rescaling the energy axis
was also observed by other groups /23/ who justified it with the
influence of the core hole. It is not clear if this is also the
reason in the present case.

Although the projected density of states of NiH is far from
constant and the broadened curve shows no arctangent behavior
the calculation locates the Fermi level at the first inflection
point of the edge (figure 6). This is not true, however, for
pure Ni because the peak at 3 eV in $D_1(E)$ leads to a displace-
ment by 0.75 eV of the first inflection point to higher energies.
The calculation, on the other hand, gives an alignment of the
K-edges of Ni and NiH as in figure 6 (same value E_o for Ni and
$NiH_{0.85}$). This means that the energy difference between the 1s
state and the Fermi level is the same in Ni and $NiH_{0.85}$ to with-
in $\pm$ 0.1 eV.

6. Conclusions

1. We have presented experimental results of K, L_1, L_2 and
   L_3 X-ray absorption edges for a number of metal hydrides.
   The K and L_1 edges of the hydrides have less structure in
   the edges than the corresponding pure metals.
2. A band structure calculation for Ni and NiH extending up to
   36 eV above E_F has been performed. The hydrogen lowers host
   states with s-character at the octahedral interstices espe-
   cially strongly.
3. The main structures in the absorption edges reflect the struc-
   tures in the projected densities of empty states ($D_1(E)$ in the
   case of the K edges in Ni and NiH). Additional effects such
   as the rescaling of the energy axis by 5 % between the mea-
   sured XANES and the absorption coefficient deduced from the
   projected densities of state are not yet understood.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6