

Lattice Site Location of Hydrogen by Use of Extended X-Ray Absorption Fine Structure

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Hydrogen shows no measurable backscattering for photoelectrons in extended x-ray absorption fine structure. When a H atom is located between an absorber and a backscatterer, however, it affects the photoelectron wave in magnitude and phase. This is demonstrated on Ni and Cr hydrides. The radial and angular information of the hydrogen position provided by this effect has a wide range of applicabilities such as the structure of metal-hydrogen systems, the trapping of hydrogen by impurities, and the determination of hydrogen bonds in molecules.

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The determination of interatomic distances and of coordination numbers by extended x-ray absorption fine structure is based on the backscattering of the photoelectron by the atoms surrounding the absorber.¹⁻³ Hydrogen with its single electron shows no measurable backscattering. Hydrogen manifests itself in EXAFS by the lattice expansion it produces in a matrix but the lattice site occupied by the hydrogen cannot be determined from the expansion. I would like to show in this Letter that the lattice site can nevertheless be determined by EXAFS. It is a well-known effect that, e.g., the fourth nearest neighbor in a fcc lattice is shadowed by the first neighbor. A photoelectron wave which is backscattered by the fourth neighbor suffers an additional phase shift and a magnification in amplitude when it passes through the potential of the first neighbor, which acts as a lens for the electron wave.¹ I show that a hydrogen atom located between the absorber and the backscatterer also acts as a lens. The corresponding changes in phase shift and the magnification in amplitude are detectable and can be used to determine the lattice site occupied by hydrogen. I demonstrate the effect on Ni and Cr hydride and then apply this effect to the problem of trapping of hydrogen by impurity atoms in a metal.

All measurements described here were done in transmission at the spectrometer ROEMO at Hasylab in Hamburg. Ni hydrides with H/Ni ratios of 0.67, 0.76, and 0.85 were prepared electrolytically. Details of the sample preparation are described by Lengeler and Zeller.⁴ The samples were stored in liquid nitrogen in order to prevent the hydrogen from escaping from the metal. Figure 1 shows the Fourier transforms of the EXAFS χk^3 for Ni and NiH_{0.85}. The Ni atoms in Ni and Ni hydride (which has the NaCl structure⁵) both form a fcc lattice. The hydrogen occupies the octahedral interstices of the fcc lattice. In order to superpose the corre-

sponding shells the abscissa for the hydride has been rescaled by $a(\text{Ni})/a(\text{NiH}_{0.85})$. This removes the effect of the lattice expansion. The values for the lattice parameters a at 77 K are 3.514 Å for pure nickel⁶ and 3.723 Å for NiH_{0.85} (see below). We were not able to prepare NiH_{1-x} with $x=0$. But samples with $x=0.33$, 0.24, and 0.15 were analyzed. A deviation of x from 0 produces a strong reduction in amplitude of the EXAFS which was found to be for the first shell:

$$\ln A_x = \ln A_0 - 4.12x. \quad (1)$$

It turns out that the value A_0 ($x=0$ or NiH) is equal to that for pure Ni.⁷ Therefore, the Fourier transforms in Fig. 1 were normalized to equal heights of the first Ni shells. Note that the third

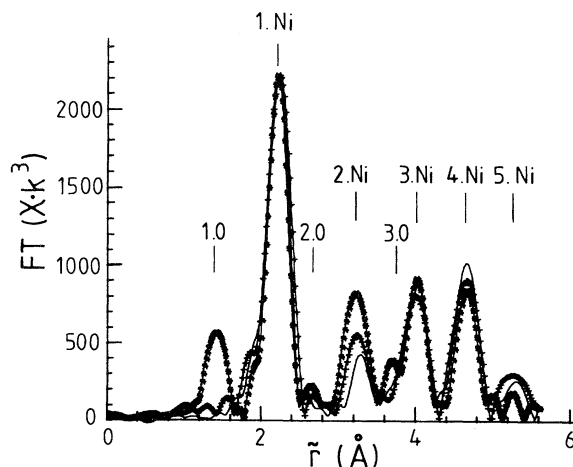


FIG. 1. Fourier transforms of the EXAFS at the K edges of Ni in Ni (solid line), NiH_{0.85} (crosses), and NiO (stars). The abscissa has been rescaled to the lattice parameter of Ni in order to align the different shells. Note the increase in magnitude of the second shell when H or O is located between the absorber and backscatterer.

and the fourth Ni shell have equal or slightly reduced heights in Ni hydride compared with Ni. But the contribution from the second shell is higher in the hydride than in pure nickel. This is a consequence of the hydrogen atom located midway between the absorber and the second neighbors. Note that there are no hydrogen atoms on the lines connecting the absorber and the third or fourth neighbors. If this interpretation is correct we expect an even stronger magnification of the second shell if we replace the hydrogen by a higher- Z element. This is what we observe in NiO (NaCl structure) when oxygen occupies the octahedral interstices, as can be seen in Fig. 1.⁸ Of course, oxygen shows in addition the usual backscattering. Three oxygen shells are visible in Fig. 1.

The results of a detailed analysis of the EXAFS of NiH_{0.85} are summarized in Table I. The phases and amplitudes used in the fitting procedure^{2,3} were taken from the corresponding shells in pure nickel. This keeps the error small when treating the photoelectron as a plane wave rather than a spherical wave.⁹ It also allows the analysis of the fourth (shadowed) shell. The values of E_0 for Ni and NiH_{0.85} were that of the first inflection point at the K edge of NiH_{0.85}.⁴ The increase in lattice parameter due to H as determined from the shells 1, 3, and 4 is 5.94%. The second neighbor gives a higher increase in lattice parameter. This increase by 0.5% or 0.018 Å is a consequence of the additional phase shift suffered by the photoelectron wave when it passes through the hydrogen. Taking into account the reduction in amplitude for $x = 0.15$ according to Eq. (1) and a mean-free-path effect due to the lattice expansion in the hydride, the coordination numbers quoted in Table I were found. Within the accuracy of the data the values for the third and fourth neighbors agree with the known values for these shells. But the coordination number for the second shell is too large by about 50%. This is a consequence of the hydrogen acting as lens for the

TABLE I. Interatomic distances r_j , coordination numbers N_j , and relative increase in distance for NiH_{0.85} compared with pure Ni.

Shell j	r_j (Å)	N_j	$\delta r_j/r_j(\text{Ni})$
1	2.632 ± 0.002	12	+5.92%
2	3.741 ± 0.003	9 ± 0.8	+6.46%
3	4.562 ± 0.003	24 ± 2	+5.99%
4	5.263 ± 0.003	12 ± 1	+5.90%

outgoing and backscattered photoelectron wave.

The analysis presented so far is based on the transfer of scattering phases and amplitudes from a model compound (Ni) which is very similar in structure to the unknown system (Ni hydride). In a second example, chromium hydride, I show that the absorber and backscatterer in the model compound can be chemically different from the system to be analyzed. In fact, in CrH the Cr atoms form a hexagonal lattice, whereas metallic Cr has a bcc structure. On the other hand, metallic Co, which differs in atomic number Z from Cr by 3, is also hexagonal. Therefore metallic Co will be used as the model for CrH. The CrH used in the present investigation was prepared in a way described by Knödler.¹⁰ The atomic ratio H/Cr determined by heat extraction was 1 within 1%. The CrH was also stored and measured at 77 K. Figure 2 shows the Fourier transform of the EXAFS χk^3 of CrH and of Co. The peak heights of the first shells are normalized to the same height. It is again obvious that the second shell for CrH is increased in amplitude by about 60% compared with Co, whereas the third and fourth shells are slightly reduced in height. According to neutron diffraction CrH has the NiAs structure¹¹ (Cr on As and H on Ni sites). X-ray diffraction, on the other hand, is not able to distinguish between the NiAs and the wurtzite structure. The values for the lattice parameters determined by x-ray diffraction which match both structures equally well are $a = 2.719$ Å and $c = 4.430$ Å. In the NiAs structure with Cr on As sites, a hydrogen is located in the middle between an absorber Cr atom

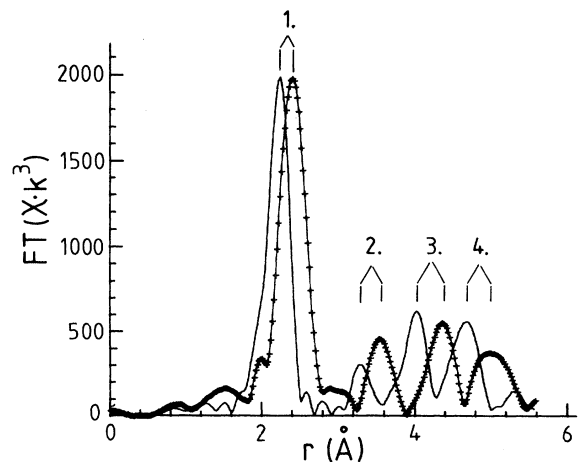


FIG. 2. Fourier transforms of the EXAFS of CrH (crosses) and Co (solid line). The Cr and Co atoms form hcp lattices. The second-shell contribution is enhanced in the hydride because hydrogen atoms are located between the absorber and its second neighbors.

and its six-second neighbors. This is just where the H is located according to Fig. 2. In the wurtzite structure, on the other hand, there is no H atom between an absorber and its second neighbor. Note that the interatomic distances and coordination numbers for any Cr shell are identical in both the wurtzite and the NiAs structure. Therefore the usual EXAFS does not allow to distinguish between these two structures. An analysis of the EXAFS of CrH with the amplitudes and phases from Co shows that the second shell gives a lattice expansion by the hydrogen which is 0.7% larger than that determined from the first and third shells. This second example shows that the stringent condition for the use of appropriate model compounds in the analysis can easily be relaxed if one takes into account that the scattering phases and amplitudes are only weak functions of Z .¹²

In a third example the new method is applied to the problem of the trapping of hydrogen by impurities in metals. The system analyzed is *Pd* Zr with 2 at. % Zr. One sample was loaded electrolytically with H up to a H/Pd ratio of 0.72. Figure 3 shows the Fourier transform of the EXAFS χk^2 for the loaded and unloaded samples. The measurements were done at 77 K. At the present hydrogen concentration the lattice is expanded by 4.1%. In this example the unloaded sample is the model for the loaded one. Again, the Fourier transforms are normalized to equal heights of the first shells. All the higher-neighbor contributions are smaller in the hydrided sample. This is also true for the second shell

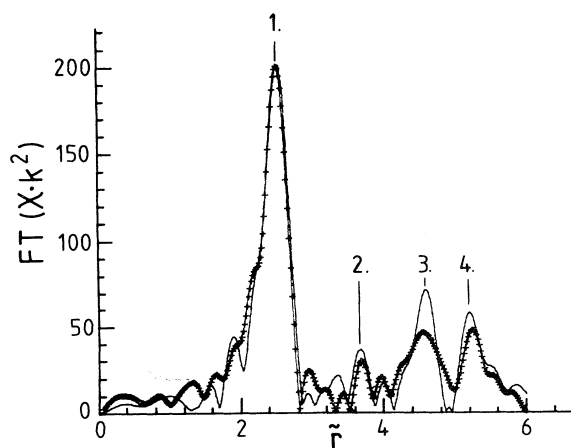


FIG. 3. Fourier transforms of the EXAFS at the K edges of Zr in *Pd* Zr (solid line) and *Pd* ZrH_{0.72} (crosses) with 2 at. % Zr. The abscissa of the hydrided sample has been reduced by 4.1% in order to correct for the lattice expansion. No hydrogen atoms occupy the six octahedral interstices next to a Zr atom in the fcc Pd lattice.

which should be enhanced if the H were trapped on an octahedral site. The present analysis shows that H is not trapped by Zr in Pd at 77 K. At the hydrogen-to-metal ratio of 0.72 chosen here we expect 4.3 hydrogen atoms next to a Zr atom if there is no interaction between Zr and H. This should be visible. Since no hydrogen is seen next to the Zr atoms we can conclude that the interaction between Zr and H at 77 K must even be repulsive. This must no longer be true at some higher temperatures. In principle, a measurement of the temperature dependence of the EXAFS can reveal the possibility of trapping at higher temperatures.

The present Letter has shown that the lattice site of hydrogen in metals can be determined by EXAFS although the backscattering from hydrogen is not observable. The method is based on the magnification of the amplitude and the shift in phase when a photoelectron passes through the hydrogen potential located on the line joining the absorber and the backscatterer. A great advantage of the technique is to give radial and angular information on the lattice site occupied by the hydrogen. It is a very useful extension of x-ray diffraction by which the metal atom positions can be detected but which is hampered for the determination of the hydrogen sites by the weak scattering power of hydrogen. The technique does not need single-crystalline samples. It is especially suited for the problem of trapping of hydrogen by impurities in metals. The trapping can affect a number of properties of the metal-hydrogen systems such as solubility, diffusion, electrical resistivity, and hydrogen embrittlement.¹³ The limit of detectability in a transmission experiment is of the order of 1 at. % impurities and 1 at. % hydrogen (when trapping occurs). In fluorescence the limit of detectability is even smaller. I feel that the technique can also be applied favorably in the determination of hydrogen bonds in certain organic compounds. Finally, I would like to emphasize that the technique is not limited to hydrogen. In a forthcoming paper I will present an investigation of the internal oxidation and the trapping of oxygen by impurities in niobium by the technique presented here.

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⁸An analysis of the second Ni shell in NiO with the phases and amplitudes of the second shell of pure Ni

gives eleven instead of six next-nearest Ni neighbors. The interatomic distance is within 0.01 \AA equal to the expected value of 4.18 \AA . The change in phase shift produced by the oxygen "lens" is compensated by a strong change in E_0 of -11.5 eV . If E_0 is not allowed to vary then the interatomic distance is increased by 0.06 \AA compared with 4.18 \AA .

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