Anomalous neutron Compton scattering cross sections in niobium and palladium hydrides

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The neutron scattering cross sections for hydrogen (H) and deuterium (D) in two metal hydrides have been studied in the Compton (or deep inelastic) scattering regime. Strongly reduced H cross sections were observed in both hydrides. This anomaly was found to depend on the characteristic scattering time, which is a function of the scattering angle and varies from about 0.1 to 1.5 fs in the present experiments. For times longer than 0.6 fs the H cross sections approached the normal, tabulated value. A smaller anomaly was observed for the D cross sections. Our experiments indicate that these, and similar anomalies earlier reported for H/D cross section ratios in water and organic compounds like polymers, amphiphiles, and organic liquids, are caused by very short-lived protonic (deuteronic) quantum correlations—which may also involve electronic degrees of freedom—of neighboring hydrogen atoms in condensed media. The neutron wavelengths are much smaller than the interparticle distances in these experiments. Still, with the support from recent calculations of neutron cross sections for quantum entangled pairs we propose that the anomalies can be explained by the fact that adjacent protons and/or deuterons in the hydrides cannot be considered as individual scattering objects. Entanglement will then modify the cross sections, for scattering times not significantly longer than the decoherence time. Possible mechanisms behind this entanglement and its decoherence are shortly described.

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I. INTRODUCTION

In recent neutron scattering experiments on partially deuterated water^{1,2} using epithermal neutrons effectuating energy transfers for the case of protons of about 5-150 eV, which results in neutron Compton scattering (NCS), the ratios between H and D cross sections were found to be strongly different from those expected from tabulated values. This was surprising, since the neutron wavelength in this case is very short (say, 0.1 Å), and no conventional explanation for these anomalies was found. It was therefore proposed that they are caused by quantum correlations between adjacent protons or deuterons (or both) such that the neutrons no longer see them as individual scattering objects.¹⁻³ For thermal neutrons, such correlation effects are well known for the specific case of H₂, but there are also recent measurements of the incoherent elastic scattering of neutrons of intermediate energy (around 0.5 eV) on crystals of KHCO₃ (Ref. 4) which show interferences that can be interpreted⁵ as resulting from quantum correlations of two protons taking part in neighboring hydrogen bonds.

If such quantum correlations indeed exist, it is relevant to ask if their effects can be observed also by other measuring techniques and in other physical systems. The most striking supporting indication of the existence of such correlations is the observation of anomalous Raman scattering on partially deuterated water by Chatzidimitriou-Dreismann *et al.*⁶ This showed a similar strong reduction of the proton/deuteron cross section ratio. It is interesting to note that Raman and neutron Compton scattering operate at shorter time scales than, for instance, thermal neutron scattering and are therefore probing very short-lived properties of the quantum systems.

The motivation of the present measurements was to search for similar evidence for short-lived quantum correlations in another type of condensed matter system, namely, the metallic hydrides. The physical properties of many of the metallic hydrides are very well known with regard to phase diagrams and crystallographic sites for hydrogen.⁷ The dynamical properties of the metal-hydrogen lattices and the mobility of hydrogen isotopes between different lattice sites have also been carefully studied, in particular for the Nb-H(D) and Pd-H(D) systems.⁸

The Nb-H(D) and Pd-H(D) systems were therefore chosen to find out if, and under what conditions, short-lived quantum correlations between light particles in condensed matter may survive. In some metal-hydrogen systems there existed already other experimental results which had not been properly explained by existing theories: One such problem was the reduced diffusion rate of protons in NbH_{0.8} when they were present as neighbors to implanted positive muons.⁹ In this and similar hydrides,^{10,11} it was found that proton jump rates were reduced by large factors (3-10), as compared to those in normal bulk hydrides. One suggested explanation¹² was that in the vicinity of the muon (which in this context can be considered as a light isotope of hydrogen), there is a destruction of proton quantum correlations which normally would serve to enhance diffusion. Another diffusion-related set of experiments had been performed on mixed hydrogen isotopes diffusing on the surface of a metal.¹³ There it was observed that when H was mixed with D (or H with T, or D with T) the diffusivity was drastically reduced as compared to that of the pure isotopes, again indi-



FIG. 1. (a) Tetragonally distorted bcc lattice of β -phase NbH_x. The H sites form chains connecting tetrahedral positions in the Nb cube faces. Full circles denote the Nb host lattice, whereas the open circles denote H or D atoms and open squares indicate the remaining vacancies. (b) Top view of the PdH_{0.5} fcc lattice. Open large circles represent the Pd atoms. Interstitial H atoms (small full circles) are situated in the [420] planes alternating with pairs of empty H sites (open small circles).

cating some kind of correlated motion in the pure systems that was destroyed by the presence of nonidentical particles. Brief reports on our results for neutron Compton scattering on the Nb-hydrides were presented earlier by Karlsson *et al.*¹⁴ and for Pd hydrides by Abdul-Redah *et al.*¹⁵

II. THE METAL HYDRIDE SAMPLES

A. Niobium hydrides

Most of our experiments on niobium hydrides were made with the hydrides in the beta phase, which is stable in NbH_x (or NbD_x) for x values approximately between 0.73 and 1.00 and in the temperature range 200–370 K. In the β phase, the bcc Nb lattice is slightly tetragonally distorted. The hydrogen takes up tetrahedral positions in the Nb cube faces and the energetically most favored H sites form chains connecting such tetrahedral sites, as illustrated in Fig. 1(a), with empty tetrahedral sites in the layers between being filled only at higher x. For temperatures below 200 K, at the x values studied here, the H- (or D-) sublattice orders such that the "strings" mentioned above are occupied by proton (or deuteron) pairs with regular spaced vacancies in between, but the lattice remains tetragonally distorted, as in the betaphase.

In the tetrahedral positions, protons or deuterons are situated in potential wells whose properties have been studied by inelastic neutron scattering. For NbH_x in the β phase, Verdan *et al.*¹⁶ obtained for the difference between the zero point vibrational level (i.e., the ground state) and the first excited state an energy of 114 meV (the corresponding value for NbD, as measured by Conrad *et al.*¹⁷ and Stump *et al.*,¹⁸ being $\Delta E^{\text{vibr}} \approx 70$ meV). Assuming approximate harmonicity between the zero-point (E_0) and first vibrational (E_1) levels of the vibration and the relations $E_0^{\text{vibr}} = \hbar \omega/2$; $E_1^{\text{vibr}} = 3\hbar \omega/2$, one obtains a position of around 50 meV above the bottom of the well for the zero-point level in NbH (and correspondingly, around 35 meV for NbD). These values will enter in the following discussion, as well as the root-meansquare values of the momentum width $\langle p_H^2 \rangle^{1/2}$ or $\langle p_D^2 \rangle^{1/2}$ of the particle vibrations. Values of $\langle p_H^2 \rangle^{1/2}/\hbar = 4.5 \text{ Å}^{-1}$ and $\langle p_D^2 \rangle^{1/2}/\hbar = 5.2 \text{ Å}^{-1}$ were determined (i) from the relation between vibrational energy and momentum spread used by Evans *et al.*,¹⁹ and (ii) from our own experiments, where the peak width in a TOF spectrum is related to $\langle p_H^2 \rangle^{1/2}$. Direct measurements of the same quantities in the present experiments (see Sec. IV A) gave the values $\langle p_H^2 \rangle^{1/2}/\hbar$ = 4.33 Å⁻¹ and $\langle p_D^2 \rangle^{1/2}/\hbar = 5.0 \text{ Å}^{-1}$. Since the difference between ground and excited state energies is in both cases of the order of 100 meV, the population of the excited vibrational states are rather small at room temperature and below.

When kept in ambient atmosphere, hydrogenated foils of Nb are covered by a thin natural oxide layer which serves as an efficient barrier for hydrogen up to temperatures of at least 450 K. The hydrogenated Nb foils, which had a thickness of 0.5 mm and an area of 30×50 mm could therefore be mounted, freely hanging in an Al frame for measurements at room temperature. For the lower temperatures the Nb foils were mounted in a thin-walled closed-cycle cryostat. In both situations, the scattering from surrounding material was kept at a minimum. NbH_xD_y hydrides with $x + y \approx 0.80$ [x =0.78, y=0; x=0.61, y=0.28; x=0.39, y=0.46; x=0.16, y=0.70; x=0.03, y=0.80] were prepared in a specialized hydrogenation setup in Uppsala²⁰ by first heating the Nb foils in vacuum at 1000 °C and then exposing them to pure H_2 or D_2 gas at a pressure of 2–2.5 bar and a temperature of 340 °C for 1.5 h. They were then used directly for the neutron scattering experiments. For the low temperature measurements a standard closed-cycle cryostat was used. The isotope ratios for the mixed hydrides were determined accurately $(\pm 2\%)^{20}$ by a mass spectrometer after outgassing.

B. Palladium hydrides

Palladium absorbs hydrogen at room temperature. The alpha-phase is saturated at about 2% H, where a β -phase hydride PdH_x starts to grow and is fully developed at x \approx 0.60. The question of local clustering of H atoms within the α phase has been discussed by Cox *et al.*²¹ who considered the stability of pairs or larger H groups within the Pd lattice. In the β phase the lattice maintains its fcc symmetry but is expanded by about 3.5%.⁷ The protons (or deuterons) occupy interstitial sites of octahedral symmetry. The β -phase hydride is also considered to be a solid solution (i.e., without H-H ordering) over the temperature and concentration range considered here. For the Pd-D system a partial ordering, with filling only of sites in alternating planes, (similar to that described for the "chains" the Nb hydrides), has been observed by neutron diffraction by Blaschko et al.,²² see Fig. 1(b), and it is probable that a similar arrangement is valid also for the Pd-H system at the H concentrations studied here.

In the octahedral sites $E_1^{\text{vibr}} - E_0^{\text{vibr}} = 68(2) \text{ meV}$ for PdH (Ref. 23) [and 48(4) meV for PdD], which corresponds to $E_0^{\text{vibr}} \approx 30 \text{ meV}$ for the zero-point vibration of H (and $\approx 20 \text{ meV}$ for PdD). The values of $\langle p^2 \rangle^{1/2}$ were estimated as $\langle p_{\text{H}}^2 \rangle^{1/2} / \hbar = 3.4 \text{ Å}^{-1}$ and $\langle p_{\text{D}}^2 \rangle^{1/2} / \hbar = 4.1 \text{ Å}^{-1}$.

The hydrogenation of the 0.5 mm thick Pd foils was done *in situ* at ISIS. The sample cans (volume 11.3 cm³), which were placed at the end of a cryostat rod, were connected to a gas system with a reference volume of 1000 cm³ and the absorbed H (or D) was monitored through the decrease of the gas pressure.

III. NCS MEASUREMENTS

A. Neutron Compton scattering

The neutron Compton scattering (NCS) technique^{24–26} (also called deep inelastic neutron scattering, DINS) uses "high energetic" (so-called epithermal) neutrons with kinetic energy up to some hundreds eV. Sufficiently intense fluxes of such neutrons are presently provided only by pulsed neutron spallation sources. Our experiments have been performed with the electron-volt spectrometer eVS of the ISIS spallation neutron source (Rutherford Appleton Laboratory, U.K.).

In this section we give an outline of basic elements of the theory of NCS. The theoretical considerations are following the works of Sears²⁷ and Watson.²⁶

The double differential cross section for the scattering of a neutron by a nucleus (of a system of N identical nuclei) is given by

$$\frac{d^2\sigma}{d\Omega dE_1} = b_M^2 \frac{k_1}{k_0} S(\mathbf{q}, \omega), \qquad (3.1)$$

where b_M is the scattering amplitude for nuclei of mass M (corresponding to a total cross section $\sigma_M = 4 \pi b_M^2$ for bound nuclei), $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1$ is the momentum transferred in the collision and $\omega = E_0 - E_1$ is the neutron energy loss (indices "0" and "1" refer to neutron states before and after the collision, and the convention $\hbar = 1$ is used here). Since the impulse approximation (IA) is valid in the present experiment, the dynamic structure factor $S_M(\mathbf{q}, \omega)$ can be accurately described by the form

$$S_M(\mathbf{q},\omega) = \int n(\mathbf{p}) \,\delta(\omega - \omega_r - \mathbf{q} \cdot \mathbf{p}/M) d\mathbf{p}, \qquad (3.2)$$

where $n(\mathbf{p})$ is the momentum distribution for the scattering nucleus and $\omega_r = q^2/2M$ the recoil energy. If the momentum distribution is isotropic the dynamic structure factor can also be described in IA by a simple scaling function $J(\mathbf{e_q}, Y)$, using the transformation²⁷

$$S(q,\omega) = \frac{M}{q} J(\mathbf{e}_{\mathbf{q}}, Y), \qquad (3.3)$$

where $Y = (M/q)(\omega - q^2/2M)$, $\mathbf{e}_{\mathbf{q}}$ is a unit vector along the direction of \mathbf{q} , and $q = |\mathbf{q}|$. The function $J_M(\mathbf{e}_{\mathbf{q}}, Y)$ is called the neutron Compton profile. The quantity $qS_M(q,\omega)$ depends only on Y and not on ω and q separately. $J_M(\mathbf{e}_{\mathbf{q}}, Y)$ is

the one-dimensional projection of the nuclear momentum distribution along the scattering vector direction.

The determination of the shape and width of this profile is the purpose of most experiments using Compton scattering. In contrast, the aim of present experiments is to determine the areas of the profile curves in order to determine neutron cross sections. This is done by comparing areas of the Compton profiles for scattering on H and D with those obtained for scattering on heavy nuclei present in the same targets.

When several different atomic masses M_i are present in the samples the neutron spectrum consists of peaks centered on different recoil energies ω_{rM} , whose widths are determined by the momentum distributions $n(\mathbf{p}_M)$ for each atomic mass. The number of counts $C(t)\Delta t$ collected in a time channel of width Δt centered at t is given by²⁸

$$C(t)\Delta t = \left[I(E_0) \frac{dE_0}{dt} \Delta t \right] [\eta(E_1) \Delta \Omega f(E_1)] \sum_M N_M \frac{d^2 \sigma_M}{d\Omega dE_1},$$
(3.4)

where $I(E_0)$ is the number of incident neutrons per cm² s corresponding to the time channel *t* with width Δt , N_M is the number of scattering nuclei with mass M, $f(E_1)$ is the energy resolution of the analyzer, and $\eta(E_1)$ is the detector efficiency.

Using Eq. (3.3), substituting the wave numbers by the corresponding velocities and incorporating the instrument resolution function in momentum space R(Y), the count rate is

$$C(t) = \frac{1}{4\pi} \frac{v_1}{v_0 q} \left[I(E_0) \frac{dE_0}{dt} \right]$$
$$\times [\eta(E_1) \Delta \Omega f(E_1)] \sum_M N_M \sigma_M M J_M(\mathbf{e_q}, Y_M)$$
$$\otimes R(Y_M), \qquad (3.5)$$

where \otimes denotes a convolution. R(Y) is a Gaussian in the case that a U foil is used as analyzing foil, and a Voigt if an Au foil is used. The following should be pointed out: It is a big advantage of the inverted geometry spectrometers (such as the eVS) that in the "foil in/foil out" difference spectrum the neutrons contributing to a scattering intensity have the same peak final energy.²⁹ Monte Carlo simulations showed that the energy dependent detector efficiency related to the finite energy resolution of the analyzer foils has only a minor effect (<1%) on the data. Therefore, the possible energy dependence of the detector's efficiency becomes irrelevant in the present physical context.

According to Eqs. (3.3) and (3.4) the fitted peaks for each mass, taken within each detector solid angle $\Delta\Omega$ (i.e., at a certain scattering angle $\theta + \Delta\theta$) are expected to be proportional to the quantities $N_{M_i}b_{M_i}^2 \equiv N_ib_i^2$ for each of the masses M_i . (To simplify notations, the subscript M may be dropped here and in the following.) The dependence on the mass ratio m/M_i (m: neutron mass) at the specific angle θ , etc., is included for each mass in the data analysis program such that the area ratios A_i/A_j presented in the following are propor-



FIG. 2. Upper part: Foil in (full line)/Foil out (dotted line) spectrum of NbH_{0.16}D_{0.70} measured at an angle θ =65°. The dips are due to resonance absorption of the gold analyzer foil (see text for more details). Lower part: Difference spectrum (indicated by the small error bars due to counting statistics) of the foil in/foil out spectra. Peaks with increasing time of flight are due to H, D, and Nb.

tional to the ratios b_i^2/b_j^2 and therefore also to the ratio of the bound nuclear cross sections σ_i/σ_j .

B. The eV spectrometer

The eV spectrometer is a time of flight (TOF) instrument. The TOF spectra are recorded with respect to the time each neutron takes from the neutron moderator (which is situated directly after the spallation target) to the detector. This time of flight of each neutron is formally given by

$$t = t_0 + L_0 / v_0 + L_1 / v_1, \qquad (3.6)$$

where t_0 is a time constant that determines which channel in the time of flight spectrum corresponds to (infinitely fast) neutrons with zero time of flight (This is determined by electronic delay times in the detector-discriminator-electronicscomputer chain), L_0 is the distance from moderator to sample (11.055 m) and L_1 is the distance from sample to detector (around 0.5 m) and v_0 and v_1 are the neutron velocities before and after the scattering process, respectively. The time of flight *t* is measured with an accuracy of around 1 μ s.

The eVS instrument is a so-called inverted geometry²⁹ spectrometer. In this experimental technique, the sample is exposed to a polychromatic neutron beam and the energy of the scattered neutrons is analyzed. For this purpose a nuclear resonance difference technique is used, which consists in the following. A foil situated between sample and detector strongly absorbs neutrons over a narrow range of energies, centered at the neutron absorption resonance specific for the nuclei in the foil material. In order to get TOF spectra allowing the analysis of intensities corresponding to the different scattering nuclei, two measurements are taken: one with the foil between the sample and detector and one with removed foil. The difference between these two spectra gives the final TOF spectrum, cf. Fig. 2. This procedure is automatic and histograms are collected alternatingly with "foil in" and "foil out" in periods of 5 min. The line shape of a measured recoil peak is governed by the momentum distribution of the nucleus, Eq. (3.3), convoluted with the line shape of the foil absorption. In our experiments presented below we used a gold foil analyzer, which has a Lorentzian shaped resonance absorption centered at 4908 meV and a half width at half maximum (HWHM) of 130 meV. The velocity of an incident neutron is determined from the measurement of the neutron TOF via Eq. (3.7) below. Another option available at the eVS instrument (which, however, was not used in the present experiments) is to use a uranium absorption resonance centered at 6771 meV with a HWHM of 60 meV, which is Gaussian shaped. This option is often used in such experiments, in which the primary goal is to determine precisely the shape of the recoil peak, rather than its integral intensity, as in our case. However, the U absorption resonance is much weaker than that of Au (roughly by a factor of 10), which necessitates considerably longer measuring times.

The scattered neutrons are collected by 32 ⁶Li doped glass detectors.³⁰ In these detectors the neutrons produce α and ³He particles when hitting the ⁶Li nuclei. The particles excite Ce ions (also doped into the glass bars, which are 25 × 200 mm each). The 190 nm photons from the Ce decay are picked up by photo multiplier tubes producing pulses of about 100 ns duration.

The events from the different detectors in each bank are collected in buffers and fed to one of the two PPFM (pingpong frame memory) units (which one to chose can be selected externally, so as to minimize the load on each of them for the specific scattering angle ranges used). The information is then sent further for histogram formation. Particular care was taken in the present experiments to avoid overloading in any of these steps, which could lead to counting losses at certain angles. Dead time losses were kept below a few percent, even at the highest counting rates used. The performance of the whole data acquisition system was also checked repeatedly by interchanging buffers and PPFM units between the different detector banks.

The detector banks of eVS were placed such that angles in the range between 30° and 80° were covered in the forward direction and 100° to 130° in the backward direction. Peaks corresponding to scattering on protons, deuterons, and heavier nuclei (from Nb, Pd, or Al containers) appear in the time regime 0–500 μ s.

The time at which the recoil peak of a specific nucleus appears in the TOF spectrum depends on the ratio of the given velocity $v_1 = k_1/m$ of the scattered neutrons to that (i.e., $v_0 = k_0/m$) of the incident neutrons. The quantity *m* is the mass of the neutron. This ratio is given by

$$\frac{v_1}{v_0} = \frac{k_1}{k_0} = \frac{\cos\theta + \sqrt{(M/m)^2 - \sin^2\theta}}{M/m + 1}$$
(3.7)

which, together with

$$q = (k_0^2 + k_1^2 - 2k_0k_1\cos\theta)^{1/2}$$
(3.8)

that holds due to momentum conservation, gives the peak position in the TOF spectrum for each scattering nucleus of specific mass M (for a detector at scattering angle θ). Therefore, the TOF spectra exhibit two features. First, the higher the mass of the scattering nucleus, the larger is the time at



FIG. 3. Measured time of flight spectrum (indicated by the error bars) of NbH_{0.16}D_{0.70} measured at an angle θ =65° as in Fig. 2 together with the corresponding fit. The three peaks correspond to H, D, and Nb (from the left to the right). Only the peak heights are fit parameters. The peak position in time of flight is known by the mass of the scatterer. The peak fixed widths are known from independent measurements; see text for more details. (Taken from Ref. 14.)

which its corresponding peak appears in the TOF spectrum (cf. Fig. 2). Second, for a nucleus of specific mass, increasing the scattering angle corresponds to a shift of the recoil peak to shorter times. The recoil peaks of H and D are well resolved for angles larger than 40°. The peak separation improves with increasing angle since the peak positions are determined by the kinematic equation (3.6). The peak widths in momentum space are fixed at the values obtained from measurements of pure niobium hydride and pure niobium deuteride by assumption. (Adding the peak width as a fitting parameter usually results in only minor modification of the peak areas.) The TOF spectra recorded at backscattering angles (to which hydrogen can not contribute) offer the possibility to resolve the peaks of higher mass, e.g., for distinguishing scattering from Pd from that of the Al container (for scattering on niobium hydrides no Al container is necessary).

Here it should be noted that the impulse approximation (IA, see Sec. III A) is well fulfilled for all scattering angles used, because the recoil energy E_r is always much larger than the vibrational energy E^{vibr} of H or D, i.e., $E_r \ge E^{\text{vibr}}$. This inequality represents the correct criterion for the validity of IA; see Ref. 26. For instance, for the scattering angle $\theta = 40^{\circ}$ one has $E_r > 3.5 \text{ eV}$ for protons and $E_r > 1.3 \text{ eV}$ for deuterons, while E^{vibr} is in both cases (see Sec. II) less than 0.1 eV. For different descriptions and various applications of the NCS technique and the eVS instrument of ISIS, see, e.g., Refs. 26,24,25,30–33.

C. Data treatment

For each nucleus of mass M the foil-in/foil-out difference TOF spectra are fitted with the aid of a Gaussian convoluted with the instrument resolution function; see Eq. (3.5) above. In the data analysis employed in our experiment, only the amplitude is a free fitting parameter to a measured TOF spectrum, i.e., the width of the fitting function is kept constant; see above. Figure 3 shows an example for a measured TOF spectrum (including error bars) and its fitted spectrum (full line).

The peak areas thus determined are proportional to the product of the total *bound* scattering cross section σ_M and the number density N_M of atoms of the mass M present in the sample, i.e.,

$$A_M \sim \sigma_M N_M \,. \tag{3.9}$$

Therefore, if the number densities for two atoms with different masses are known, the following equation holds strictly:

$$\frac{A_i}{A_j} = \frac{N_i \sigma_i}{N_j \sigma_j}.$$
(3.10)

Since the conventionally expected values of the bound scattering cross section σ_i and σ_j are given in standard tables,²⁴ the validity of the basic Eq. (3.10) is directly subject to experimental test.

Very recently, Blostein et al.³⁴ criticized the widely used expression for the experimentally observed spectral intensity in terms of a convolution (see Sec. III A) and proposed a procedure based on the complete absorption cross section of the used absorption foil (Au in the case of present experiments). They concluded that the usually employed data analysis procedure based on the "convolution formalism" leads, among others, to incorrect values of peak areas in the case of two (or more) overlapping recoil peaks, in particular those of H and D. However, Chatzidimitriou-Dreismann et al. demonstrated very recently by presenting new experimental results on D_2O and the equimolar H_2O-D_2O mixture³⁵ that the objections of Blostein et al. concerning the peak areas are of no relevance for our present and previous experimental results and the cross-section anomalies observed. In particular, the work of Ref. 35 has refuted the criticism³⁴ concerning the evaluation of H/D intensity ratios from partly overlapping H and D peaks in the TOF spectra recorded with the eVS instrument. It was found³⁵ that for pure D₂O, where the D/O intensity ratio could be obtained instead of D/H, the cross section ratio was close to normal (which means that the anomaly found in Ref. 1 lies mainly in the H cross section), and that for the equimolar H₂O-D₂O mixture the H/O peak ratio was 12.5 ± 1.5 instead of the conventionally expected value 19.4. This finding represents a 35% reduction (which cannot be explained by H/D overlap), and is in agreement with the information from the H/D peak ratios reported for the same mixture in the original Ref. 1. For the presently studied metallic hydrides, peak-overlap problems are of much less relevance, as has been very recently demonstrated by Abdul-Redah et al.³⁶

H cross section reduction in neutron Compton scattering has now also been observed for several other materials by comparing areas of clean and well resolved scattering peaks in the eVS instrument, such as for H/Nb (Refs. 14,15) and H/C (Refs. 37–40).

D. The scattering times

Neutron Compton scattering (NCS) is a "fast" process. This is understood already from the amount of energy transferred [$\tau \sim \hbar/(\text{few eV})$], and was pointed out in the discussion by Sears.²⁷ Sears²⁷ and Watson²⁶ analyzed the NCS-situations in detail for scattering at different angles (corresponding to different amounts of wave-vector transfer q). They defined a scattering time τ_s , which can be approximated as

$$\tau_s(\theta) \approx \frac{M\hbar}{q(\theta) \langle p_M^2 \rangle^{1/2}},\tag{3.11}$$

where $\langle p_M^2 \rangle^{1/2}$ is the width of the momentum distribution of the scattering nuclei and $q(\theta)$ the momentum transfer at scattering angle θ . The quantity $\langle p_M^2 \rangle^{1/2}$ can be estimated from the vibrational energies of H (or D) in the interstitial positions in the hydride, or can be taken directly from the momentum width in the NCS spectra, as discussed in Sec. III A.

The ratio (3.11) can also be expressed in terms of $\hbar q_1 = \sqrt{2mE_1}$, which is the momentum corresponding to the final neutron energy $E_1 = 4.92$ eV. With the help of the relation [cf. Eq. (3.7)]

$$\frac{p_1}{p_0} = \frac{\cos \theta + \sqrt{(M/m)^2 - \sin^2 \theta}}{M/m + 1}$$
(3.12)

and

$$\frac{\hbar^2 q^2}{2M} = \frac{p_0^2}{2m} - \frac{p_1^2}{2m}$$
(3.13)

one obtains, for the transferred momentum for scattering on protons

$$\hbar q_H = \hbar q_1 \tan \theta \tag{3.14}$$

and for scattering on deuterons

$$\hbar q_D = \hbar q_1 \frac{2\sqrt{3 - z\cos\theta}}{z},\tag{3.15}$$

where

$$z = \cos \theta + \sqrt{3 + \cos^2 \theta} \tag{3.16}$$

and $q_1 = 48.6 \text{ Å}^{-1}$.

The scattering time τ_s can be seen as an integration time, over which possible time-dependent phenomena are averaged. By Eqs. (3.11) and (3.14)–(3.16) the θ dependence can be transformed to a time dependence using the equation

$$\tau_s(\theta) = c \frac{q_1}{q(\theta)} 10^{-15} \text{ s,}$$
(3.17)

where the constant *c* depends on the mass and the vibrational properties of the scattering hydrogen nuclei in the metal considered. For H in Nb it has the value c = 0.76, for D in Nb c = 1.32, for H in Pd c = 1.01, and for D in Pd c = 1.68.

The time $\tau_s(\theta)$ is the effective time window which is set by the scattering angle θ , the momentum transfer and the potential the scattering particle is subject to. The information obtained from scattering angles in the range $40^\circ - 80^\circ$ correspond to typical observation time ranges from 2×10^{-16} s to 1.5×10^{-15} s for protons in the metal hydrides.

IV. EXPERIMENTAL RESULTS

A. Niobium hydrides

As an example of the data obtained with the eVS we present in Fig. 3 the time-of-flight (TOF) spectrum for one of the Nb-hydrides containing both protons and deuterons, NbH_{0.16}D_{0.70}, as observed at one particular angle $\theta = 65^{\circ}$. The peaks correspond, with increasing TOF, to scattering from H, D, and Nb. As explained in Sec. III B these peak areas A_M are proportional to the number of nuclei of mass M present in the sample, multiplied by their effective cross section σ_M . The measured ratios

$$A_{\rm H}/A_{\rm Nb} = x\sigma_{\rm H}/\sigma_{\rm Nb}, \quad A_{\rm D}/A_{\rm Nb} = y\sigma_{\rm D}/\sigma_{\rm Nb},$$

 $A_{\rm H}/A_{\rm D} = (x\sigma_{\rm H})/(y\sigma_{\rm D})$ (4.1)

provide values for $\sigma_{\rm H}/\sigma_{\rm Nb}$, etc., with an accuracy determined by the uncertainties in A_M , and x and y, respectively. In the standard procedure a weighted average of the results from the 2×16 spectra (obtained for different angles) is evaluated. The results obtained in this way for the Nb hydrides were tabulated in Ref. 14. The ratio $\sigma_{\rm H}/\sigma_{\rm Nb}$ obtained from Eq. (4.1) varied from 11.2(9) to 10(2) going from pure NbH ($x_{\rm D}$ =0) to $x_{\rm D}$ =0.8, and the ratio $\sigma_{\rm D}/\sigma_{\rm Nb}$ from 1.09(3) for $x_{\rm D}$ =0.96 to 0.9(1) for $x_{\rm D}$ =0.31. The errors given here are purely statistical.

It is seen that the data for the cross section ratios are reduced by more than 20% for $\sigma_{\rm H}/\sigma_{\rm Nb}$ and by about 10% for $\sigma_{\rm D}/\sigma_{\rm Nb}$ as compared to the conventionally expected cross section ratios $(\sigma_{\rm H}/\sigma_{\rm Nb})_{\rm conv} = 81.67/6.25 = 13.1$ and $(\sigma_{\rm D}/\sigma_{\rm Nb})_{\rm conv} = 7.63/6.25 = 1.22$. They represent therefore an anomaly, similar to the anomaly which has been found for the first time by Chatzidimitriou-Dreismann *et al.* in liquid H₂O-D₂O mixtures¹ and later also in D₂O solutions of urea,³ solid polystyrene,³⁷ liquid benzene,³⁸ and solutions of iso-C₄E₁ in D₂O.³⁹ In this context it should be stressed that metal hydrides, such as the polystyrene samples, allow a possibility to determine the degree of anomaly separately for H and D scattering. The Nb hydrides were, similar to the polystyrene foils mentioned earlier, freely hanging in the scattering chamber without the need of a container.

It is also interesting to observe that the reduction in the H cross section as observed in the hydrides is much larger than that of the D cross section, which is in line with the interpretation that the strong reduction of $\sigma_{\rm H}/\sigma_{\rm D}$ observed in H₂O-D₂O mixtures¹ is mainly due to a reduced effective H-cross section, rather than a change of D cross section. This has also been shown by Chatzidimitriou-Dreismann *et al.* in an experiment on D₂O and the equimolar H₂O-D₂O mixture very recently.³⁵ So the area ratios of $A_{\rm H}/A_{\rm Nb}$ and $A_{\rm D}/A_{\rm Nb}$ are free from overlap corrections.

As stressed already, $A_M/A_{M'}$ ratios calculated in the way described above are expected to be independent of scattering angle. This seems indeed to be the case for the pure deuteride NbD_{0.80}, as seen in Fig. 4, but similar plots of the data for



FIG. 4. The cross section ratio σ_D/σ_{Nb} of NbH_{0.16}D_{0.70} vs scattering angle θ . The horizontal line indicates the conventionally expected value σ_D/σ_{Nb} =7.63/6.25=1.22. An angle independent small reduction of σ_D/σ_{Nb} with respect to this value is observed. (Taken from Ref. 14.)

the H-containing samples (see Fig. 5) exhibit striking deviations from this expectation. They show a clearly decreasing trend with increasing scattering angle, reaching reductions up to 40% for the highest scattering angles. It is also notable that for the pure NbH_{0.78} the curve starts out with normal values of $\sigma_{\rm H}/\sigma_{\rm Nb}$ but has strong deviations already at scattering angles around 55°–60°. Such strong angle dependent deviations are not existent in data from liquid water,¹ solid polystyrene,³⁷ liquid benzene,³⁸ and amphiphiles,³⁹ thus indicating that the different dynamics related to different condensed matter environments cause different anomalies.

Since high scattering angles correspond to short observation times, it was now natural to analyze the data in terms of scattering time, by transforming the θ dependence to a dependence on the scattering time τ_s using Eq. (3.17). The results for the NbH_{0.78} sample are displayed in Fig. 6, where data taken at room temperature as well as at 20 K are shown. It can be seen that H nuclei in NbH_{0.78} show an anomalous neutron cross section only for observation times shorter than



FIG. 5. The cross section ratio $\sigma_{\rm H}/\sigma_{\rm Nb}$ of NbH_{0.78} vs scattering angle θ . The horizontal line indicates the conventionally expected value $\sigma_{\rm H}/\sigma_{\rm Nb}$ =81.67/6.25=13.1. A strong angle dependent reduction of $\sigma_{\rm H}/\sigma_{\rm Nb}$ with respect to this value is observed. The conventionally expected value is approached below $\theta \approx 50^{\circ}$.



FIG. 6. The cross section ratio $\sigma_{\rm H}/\sigma_{\rm Nb}$ of NbH_{0.78} vs scattering time τ_s at T=298 K (full squares) and T=20 K (open squares) after transformation of the scattering angle θ to τ_s according to Eq. (3.11). $\sigma_{\rm H}/\sigma_{\rm Nb}$ is anomalously reduced up to 0.6 fs and assumes then the conventionally expected value (horizontal line). No differences are observed between measurements at these largely differing temperatures. (Taken from Ref. 14.)

around 0.6×10^{-15} s. This is a clear indication of the existence of some kind of fast decaying state of the H system in this hydride. For the mixed hydrides, similar plots of the effective H/Nb cross section,¹⁴ see Fig. 7, show a similar strong reduction at short times but with a slower increase approaching the conventional value. The proposed, possible character of the anomalous state will be discussed further on, but it is understood already at this point that such reductions in cross section can only be imagined if the scattering is not by individual nuclei but by quantum correlated ones; see also Ref. 1. According to Karlsson and Lovesey⁴¹ the coherence length of the neutrons may still be long enough (about 2.5 Å in the present setup) to show interference from different H sites,⁴² although the de Broglie wavelength of the neutrons used here is of the order of 0.1 Å.



FIG. 7. The cross section ratio $\sigma_{\rm H}/\sigma_{\rm Nb}$ of some of the various mixtures of NbH_xD_y vs scattering time τ_s after transformation of the scattering angle θ to τ_s due to Eq. (3.11). $x_{\rm D} = n_{\rm D}/(n_{\rm H} + n_{\rm D})$ indicates the mole fraction of D and x indicates the number density fraction of hydrogen with respect to that of the metal lattice. $\sigma_{\rm H}/\sigma_{\rm Nb}$ is anomalously reduced up to 0.6 fs and assumes then the conventionally expected value (horizontal line).



FIG. 8. The measured cross section ratio $(\sigma_{\rm H}/\sigma_{\rm Pd})_{\rm exp}$ of PdH_{0.54} normalized by the conventionally expected value $(\sigma_{\rm H}/\sigma_{\rm Pd})_{\rm conv}$ vs scattering angle θ . A strong angle dependent reduction of $\sigma_{\rm H}/\sigma_{\rm Pd}$ with respect to this value is observed. The conventionally expected value is approached below $\theta \approx 60^{\circ}$ which differs from the angle dependence of the niobium hydride; see Fig. 5.

As it was expected that measurements of the temperature dependencies may help to elucidate the character of the present anomalies, most samples were also run at 80 and 20 K. Within experimental error no temperature dependencies were found for $\sigma_{\rm H}/\sigma_{\rm Nb}$ in any of the mixtures (see Fig. 6 for an example), similar to earlier low temperature experiments on H₂O/D₂O.^{43,44} The implications of this observation will also be discussed in Sec. VI.

B. Palladium hydrides

Work with Pd hydrides requires hydrogenation "in situ" since the metal surface does not develop a protecting oxide as for the Nb hydrides. The Pd-metal sample, a disc of 60 mm diameter, 0.5 mm thick, was placed in an Al container with wall thickness 0.5 mm which was connected to a hydrogen gas system with a maximum allowed pressure of 2.0 bar. The whole arrangement was placed on the cold finger of a liquid He cryostat. The amount of hydrogen absorbed after an initial connection to a H_2 (or D_2) reservoir could be determined only from the decrease of pressure in the calibrated volume (including a relatively complicated tubing system). From the absorption enthalpy curves for the Pd-H system it is expected that the H concentration should stabilize at $PdH_{x\approx0.60}$ where the pressure-composition diagram has a sharp kink upwards. This is expected to happen for pressures below the initial pressure used here. However, the pressure decrease actually measured corresponded to somewhat lower values $PdH_{x\approx0.53}$ (the values calculated from the pressure change might therefore be affected by uncertainties in pressure and volume calibration).

Several sets of runs were made for this pure Pd-H hydride at room temperature, using different setups of detectors and electronics as described below in section IV C (control experiments). The results of these separate runs were always consistent and one of the data sets is presented in Fig. 8 where $A_{\rm H}/A_{\rm Pd}$ is given as function of detector angle θ . This curve has a characteristic plateau at low detector angles, falling off relatively abruptly for $\theta > 60^{\circ}$ (i.e., at a considerably higher angles compared to the corresponding Nb-H curve,



FIG. 9. For comparison, the experimental ratio $(\sigma_{\rm H}/\sigma_{\rm C})_{\rm exp}$ in polystyrene normalized by the conventionally expected value $(\sigma_{\rm H}/\sigma_{\rm C})_{\rm conv}$ vs scattering angle is shown. Data are taken from Fig. 2 of Ref. 37. In contrast to the results on the hydrides of niobium and palladium no angle dependence is visible here within experimental error, which indicates that the conventional angle dependence being inherent to scattering intensity [see, e.g., Eqs. (3.3) and (3.8)] is correctly included in the data analysis procedure

Fig. 5). For comparison the experimental ratio $(\sigma_{\rm H}/\sigma_{\rm C})_{\rm exp}$ in polystyrene normalized by the conventionally expected value $(\sigma_{\rm H}/\sigma_{\rm C})_{\rm conv}$ vs scattering angle is shown in Fig. 9. These data were taken from Fig. 2 of Ref. 37. In contrast to the results on the hydrides of niobium and palladium no angle dependence is visible in the polymer (polystyrene) sample within experimental error, which indicates that the conventional angle dependence being inherent to the scattering intensity [see, e.g., Eq. (3.3)] is correctly included in the data analysis procedure. The constancy of $(\sigma_{\rm H}/\sigma_{\rm C})_{\rm exp}$ in the polymer sample is related to the fact that these data fall on a lower time scale because of a larger $\langle p_{\rm H}^2 \rangle^{1/2}$ factor in Eq. (3.11). The polymer data show also a reduced H cross section, but no transition to the normal value within the short time range covered (<0.5 fs).

When converted to a scattering time dependence $\tau_s(\theta)$ the drop of the scattering intensity for the Pd-H sample turns out to correspond to the same $\tau_s \approx 0.6$ fs as in the Nb-H case, since the conversion factor for the Pd system is different (see Sec. III C). The absolute values derived for the effective cross section ratio $\sigma_{\rm H}/\sigma_{\rm Pd}$ depend on the actual H concentration. With the composition $PdH_{0.53}$ calculated from the pressure data the long-time saturation value of $\sigma_{\rm H}/\sigma_{\rm Pd}$ $=A_{\rm H}/(0.53A_{\rm Pd})$ comes out about 15% higher than the tabulated cross section ratio 16.0. The saturation value of $A_{\rm H}/A_{\rm Pd}$ corresponds actually more closely to the composition PdH_{0.6} expected from the thermodynamic data. To avoid this uncertainty, the Pd-H data were instead normalized by dividing all points $A_{\rm H}/A_{\rm Pd}$ by the saturation value for long times (i.e., the mean of data taken for $\theta < 50^{\circ}$). These data are compared with the corresponding values of $NbH_{0.78}$ in Fig. 10.

The information from Fig. 10 is interesting. Large cross section anomalies exist for neutron scattering on protons in both materials; for Pd-H even somewhat larger than for Nb-H. The time within which they disappear is very similar, about 0.6 fs. A run at 4 K for the Pd-H sample (not shown here) showed only minor differences except perhaps at the



FIG. 10. The cross section ratio $\sigma_{\rm H}/\sigma_{\rm Pd}$ of PdH_{0.54} and $\sigma_{\rm H}/\sigma_{\rm Nb}$ of NbH_{0.78} vs scattering time τ_s after normalization with their corresponding conventional values for comparison. Despite their different angle dependence behaviors (see Figs. 5 and 8), the same dependence on τ_s is observed. (Taken from Ref. 15.)

highest scattering angles (= shortest times) which showed a slight tendency towards higher anomalies than at room temperature. This observation was also in agreement with the previous experiments on the Nb-H system. In summary, within present experimental error, there is no significant difference between the run at T=4 K and that one at room temperature.

A few experiments were performed with deuterated Pd, but difficulties in sample preparation allowed only a limited set of data to be obtained. They indicate a slowly decreasing $\sigma_{\rm D}/\sigma_{\rm Pd}$ ratio in an angular range between 30° and 80°, which corresponds to $\tau_s \approx 1.0-3.1$ fs.

Data from backscattering angles ($\theta > 120^{\circ}$) were necessary since for these angles the peaks corresponding to Pd and Al (in the cans) could be partially resolved in the TOF spectra. This is because a calculation based on the sample and sample holder geometry cannot be accurate enough to estimate the ratio of different masses covered by the neutron beam.

C. Control experiments

Since the present results deviate strongly from conventional expectation, several control experiments were carried out in direct connection to the collection of the data presented above. In particular, it was important to check the data for the higher scattering angles ($\theta > 55^\circ$) for which the H cross section data show a strong angular dependence.

In this context it should be remembered that the TOF spectra, as that shown in Fig. 3, are the results of a subtraction of an Au-resonant spectrum from a nonresonant one in the "foil-in/foil-out" operation (see Fig. 2). According to the kinematic relation (3.9) the H peak moves from a position at 210 μ s in the TOF spectrum at 55° to 100 μ s at 75°, (which was the highest angles used for present H data). It might therefore be suspected that counting losses could affect the evaluation of the areas $A_{\rm H}$ more for the higher angles than for the lower ones and several possible causes for such losses

were considered. They might occur in the neutron detectors themselves, in the data buffers and in the electronics performing the histogram formation. The dead times at each of these steps were studied carefully and the maximum relative errors estimated at the actual counting rates in the low TOF part of the spectra. The sample thickness was chosen such as to keep these maximum uncertainties at the level of a few percent. (A preliminary run with double sample thickness, and therefore double counting rate, did not deviate appreciably from the later, main runs.) As an additional security, the detector banks covering the higher angles were always connected to the histogramming units that had the least counting load. Several spectra were taken at the same sample and geometric conditions, but with interchange of detectors or electronic acquisition units, in order to track down the action of possible faulty or overloaded components. No systematic differences could be observed in the data obtained.

Other possible causes for systematic errors would come from multiple scattering in the target foils (and for the case of Pd hydrides the scattering from the Al cans). A selfevident test for sample thickness effects is to turn the target foils with respect to the incoming neutron beam and the detector banks such that both in- and outgoing neutrons penetrate a minimum of matter. As an example of control experiments the plane of the PdH metal hydride foil was changed from 90° to 60° with respect to the incoming beam. The variation of the $A_{\rm H}/A_{\rm Pd}$ area ratios with detector angle remained unchanged, within statistical errors. This confirmed the results of Monte Carlo calculations of the effect of multiple scattering (see below) which showed that this contribution is very small and is distributed evenly over the TOF spectra and could not give rise to any strong anomaly in the peak ratios; see Sec. IV D below.

In a different kind of control experiment, samples with different material characteristics were introduced, in between runs with the metal hydride foils, with no changes whatsoever of detectors or electronics. These comparison targets were selected to give about the same counting intensities as in the main experiments. One of these was a mixed H₂O-D₂O sample, with known characteristics from Ref. 1 and many other measurements.³⁸ Another one used in connection with our experiments on Pd hydrides was a freely hanging foil of polystyrene, as recently reported by Chatzidimitriou-Dreismann et al. in Ref. 37. The polystyrene data are essentially independent of detector angle,37 while the $A_{\rm H}/A_{\rm Pd}$ data fall off strongly at higher scattering angles, although the same experimental setup has been used. This is a direct confirmation that the drop of the H cross section in $PdH_{0.6}$ is not the result of counting losses (or faulty background subtraction) in the H peaks of the TOF spectra at low flight times (high scattering angles).

D. Monte Carlo simulations of multiple scattering

The data treatment of the experiments (see Sec. III C) makes use of the expressions (3.1)-(3.10) which are based on single neutron scattering events only. To find out to what extent multiple scattering (MS) in the samples could influence the results, a Monte Carlo program (DINSMS), available



FIG. 11. (a) Shown is the geometry of the scattering process as it occurs once (full line arrows) and twice (dashed line arrows) for the Monte Carlo simulations of multiple scattering probabilities which are as follows: (i) Single scattering: The neutron enters the sample at point A under an angle ϕ , is scattered by the nucleus (C) and is deflected by a scattering angle θ and leaves the sample at point E. Otherwise it leaves the sample at point B without interaction. (ii) Double scattering: After being scattered by nucleus C, the neutron hits a second nucleus (D) before leaving the sample at point F and gets detected by the same detector that has detected the neutron which has been scattered once. (b) Shown are the single scattering (full line) and the multiple scattering (dotted line) time of flight spectra of PdH as simulated with the Monte Carlo Method for a scattering angle $\theta = 72.5^{\circ}$. For the sake of visibility, the multiple scattering is multiplied by a factor of 10. As can be seen, the multiple scattering contribution is very small and rather evenly distributed over the time of flight.

at ISIS, was used. The MS program calculates the attenuation length $\mu_0(v_0)$ for each incident velocity v_0 , based on tabulated neutron scattering and absorption cross section data.⁴⁵ For a recent application of the simulation program, see Ref. 46.

The samples used in the present experiments are thin metal foils of thickness $D \le 0.5$ mm, placed either perpendicular or with a tilt angle of ϕ degrees with respect to the incoming beam (Fig. 11).

For the calculation of the multiple-scattering corrections, the ratio between "twice" (A-C-D-F) and "once" (A-C-E)

scattered neutrons was calculated. It was found that, with the relatively thin metal foils used in the present experiments, the multiple scattering intensity was always small in comparison to that for single scattering. One example of these simulations is presented in Fig. 11, where the multiple scattering contributions from the PdH sample (the thickest one in this series) was compared with the single scattering for a TOF spectrum taken at θ =72.5°. Even at this high angle, where the neutron path length in the sample is relatively large, the multiple scattering contribution (dotted curve) is small, and almost negligible compared to the anomalies found in the H/Pd peak ratios discussed in the present paper.

V. REMARKS ON THEORETICAL INTERPRETATIONS

As is evident from the discussions presented above, no conventional explanation for the observed anomalies has been found.

(a) As explained above, Eq. (3.10) is strictly valid within conventional theory.

(b) The area ratios $A_{\rm H}/A_M$, where *M* represents scattering on a heavy nucleus, have been obtained under clean conditions (no problems with overlapping tails, which could have caused problems of the type discussed in Ref. 34; this is particularly clear for scattering angles larger than, say, 50°, where the peaks are widely separated). In the Nb-H experiments there is no background due to containers, etc that could have caused uncertainties in these ratios.

(c) The program for calculation of areas at the eVS spectrometer has been carefully checked and it was found that the approximations used in it cannot lead to errors exceeding a few percent, i.e., far below the anomalies observed. In this program, all peaks (including the high-energy H peak) are composed of all events, with separate initial neutron energies E_0 and momentum transfers q. The peaks are all found to be well described by Gaussians in the J(Y) representation. This program has also the option to take into account final state effects (FSE) which lead to distorted Gaussians in the J(Y) representation (see Sec. III C), but our analysis has shown that FSE play no role in the determination of peak areas [although they usually affect the shape of J(Y)].

(d) Multiple scattering has been minimized and the remaining contribution was calculated to be far beyond the 20% anomalies observed (see Sec. IV D).

(e) Possible errors due to dead-time losses in detectors and data handling have been found to be negligible both by specially dedicated experiments and by measuring on other samples which do not show strong angular dependencies under similar counting rate conditions

Therefore, the reason for the anomalies observed here and in experiments on other materials (water, organic liquids, polymers, etc.) must be sought on a deeper level. To interpret anomalies observed with Raman scattering in liquid water,⁶ a first theoretical model of scattering from entangled particles (i.e., OH oscillators) was proposed by Chatzidimitriou-Dreismann *et al.*,⁶ which was based on exchange correlations. Further theoretical models based on quantum correlation effects between the scattering particles have been developed by Karlsson and Lovesey^{47,41} and by Chatzidimitriou-Dreismann *et al.*^{40,48} These theories have in common that cross section losses observed by NCS are due to quantum entanglement of scattering particles, but differ concerning the assumed reason for the entanglement as well as the role that decoherence plays.

In the models by Karlsson and Lovesey47,41 and Chatzidimitriou-Dreismann et al.6 it is assumed that exchange correlations are the dominating reason for entanglement (i.e., the nonseparability of the wave functions for different scattering particles), and calculations are carried out starting from purely exchange correlated states of two fermionic (protons or OH oscillators) or two bosonic systems (deuterons of OD oscillators). In Refs. 47,41 this was shown to result in strong NCS cross section reductions for proton pairs (down to 1/3 of the standard value when the particle vibrations are isotropic with respect to the transferred momentum q in Compton scattering) and a smaller reduction for deuteron pairs. The same model has recently been used by Karlsson⁴⁹ for a quantitative explanation of the $\sigma_{\rm H}/\sigma_{\rm D}$ anomalies in water observed in the original NCS experiment of Chatzidimitriou-Dreismann et al.¹ Effects of decoherence were essential in the model of Ref. 6 but were not introduced in the model of Refs. 47,41. In Ref. 49, decoherence effects were added by Karlsson, but were found to destroy the effects of the exchange correlations only for times longer than around 20 fs, a number determined by the characteristic fluctuations in water. This model has not yet been developed for the more complicated proton configurations (and decoherence mechanisms) in systems like the presently studied metallic hydrides, but anomalies similar to those in the simpler system are expected to exist, although of lower magnitude.

The observation of strong NCS anomalies even in materials containing tightly confined protons in covalent C-H bonds^{37,39,38,40} motivated an associated theoretical model by Chatzidimitriou-Dreismann *et al.*, ^{37,40,48} in which quantum entanglement is created by the dynamics of interacting systems (e.g., protons "dressed" with electronic degrees of freedom). If the interaction Hamiltonian $V_{\alpha\beta}$ —describing interparticle and/or particle-environment interactions-does not commute with the one-particle effective Hamiltonians H_{α} and H_{β} of the single particles, then the complete evolution operator $U_{\alpha\beta}(t) = \exp[-it(H_{\alpha}+H_{\beta}+V_{\alpha\beta})/\hbar]$ does not factorize into terms describing the individual dynamics of each of the particles, which leads to entanglement between the particles.^{38,39} Further interactions with the environment cause decoherence. The point now is that entanglement alone is not sufficient to explain the NCS results. Instead, both effects of entanglement and decoherence, taken together, appear to be the cause of the reductions of observed cross sections of H.^{37,40,48} Moreover, as already theoretically predicted, ^{37,39,38} anomalous reductions of cross sections can appear even if exchange correlations are absent. (A NCS experiment to test this crucial point is under progress.)

VI. DECOHERENCE TIME

The gradual disappearance of the anomalies for longer scattering (or observation) times in Figs. 6, 7, 10 is interpreted as an effect of quantum decoherence. In condensed matter systems, coherence is expected to be lost very much faster than in the systems studied by quantum optics (where coherence can be preserved over times of the order of microseconds).

Order-of-magnitude estimates can be obtained from the expression for the decoherence rate Λ given by Joos and Zeh (see Ref. 50)

$$\Lambda = 1/\tau_{dec} = \kappa k_a^2 n |r' - r|^2, \tag{6.1}$$

where |r'-r| is the spatial extension of an "entangled" microscopic quantum system, *n* the number of quanta hitting it per time unit, and k_q the momentum of such quanta (κ is a constant of the order of 1). A quantum object with the extension of a few Å, embedded in a solid with a typical phonon spectrum, has been estimated¹⁴ to lose coherence in a time less than 10^{-15} s.

Generally, in the absence of external perturbations the decoherence time is determined by the interaction of the entangled system with "the rest of the world," i.e., by collisions with phonons, electrons, etc. in thermal equilibrium with the system, and is expected to show a temperature dependence.

Comparing the low- and high-temperature results for NbH_{0.78} it is noted that the data in Fig. 6 for 20 and 300 K practically coincide. A very similar time dependence was also seen for Pd-H at room temperature, see Fig. 10. This is an indication that the time for losing the coherence (i.e., the decoherence time τ_{dec}) is not set by thermal processes in the present type of experiments, but probably (i) by characteristic response times of electron densities surrounding the scattering nuclei (see Refs. 39,38) and/or (ii) by the perturbations caused by the measuring process (i.e., the neutron-proton collision) itself. For example, it is to be expected that in the Compton scattering, which is a violent process, spatial quantum coherence between two protons (or deuterons) will be destroyed as soon as one of them starts to leave the equilibrium position, producing excitations in the metal hydride lattice and/or electronic excitations in the surrounding equilibrium electron density. With the recoil energies typical for the present experiments, the first fs corresponds to motion over distances of 0.1-1 Å. Phonons can be excited in the metal and H sublattices (and also in the D sublattices, in the mixed hydrides). A dependence of the coherence loss on the composition of the hydrides (as visible from Fig. 7 for the NbH_xD_y system) is therefore not unexpected, since the phonon densities of states are considerably different for NbH, NbD, and the NbH_xD_y mixed hydrides. It is conceivable that the strong local perturbation associated with the recoil is more likely to excite the highest energy modes (which are those of the H-sublattice vibrations) than the less energetic ones. This is a hypothesis that may explain why the transition to "normal" cross sections is faster for NbH_{0.78} than for the NbH_xD_y samples.

Here a comparison should be made with the experiments on polystyrene (presented by Chatzidimitriou-Dreismann *et al.* in Ref. 37, see also Ref. 38) and used here as reference sample in our control experiments (see Sec. IV C) and also with the earlier data on liquid water,¹ which both showed large cross sections anomalies but only weak dependence on scattering angle θ . When the *q* dependence is converted into a τ_s dependence by Eq. (3.11), for these materials the observations turn out to fall in the 0.05–0.5 fs range because of the essentially higher momentum spread $\langle p_{\rm H}^2 \rangle^{1/2}$. These systems are probably observed, in the NCS experiments using the Au foil, over a time interval which is never much longer than the decoherence time.

VII. CONCLUSIONS

The anomalous neutron cross sections observed here and in our previous works (e.g., Refs. 1,3,14,15,37,39,38) do not seem to be possible to explain without a considerable conceptual change in the conventional quantum description of condensed matter systems. The main reason why the explicit introduction of entanglement in condensed matter systems has not been necessary before is that very few experimental methods work on time scales where its effects become observable. The eVS instrument at the ISIS neutron spallation source, Rutherford Appleton Laboratory, is unique in the sense that it has sufficient intensity to allow studies of the scattering intensity for scattering times in the fs (and sub-fs) range. With the present studies in the sub-femtosecond time range it has become possible to show that the anomalous cross sections are connected with very short-lived, "anomalous" states of the scattering particles.

The exact character of these scattering states remains to be clarified, but it seems clear that the protons (or deuterons) in the metal hydride systems studied here (and in other systems, e.g. liquid water,^{1,35} solid polysterene,^{37,38} liquid benzene,³⁸ amphiphilic molecules,³⁹ etc.) can no longer be regarded as a collection of individual scatterers. The reductions observed in the cross sections must be related to (i) quantum phase relations in the amplitudes of different scatterers, giving rise to interferences^{47,41} and/or (ii) an interplay of (two- or many-particle) quantum entanglement and deco-

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herence between scatterers and other degrees of freedom of their "environment" fulfilling relation (5.2),^{38,39} see the short theoretical considerations presented in Sec. V. The present results are also giving support to earlier, less clear-cut indications of the existence of unconventional quantum states of protons in condensed matter, such as indicated by the results from Raman light scattering,⁶ from elastic neutron scattering with lower momentum transfer (Ikeda and Fillaux⁴), from various proton transfer processes in condensed matter,^{51,52} and from the observation of coherent superpositions of states of single positive muons in metals.⁵³

In addition to addressing the question of the nature of these short-lived quantum states, the present experiments have also pointed to other fundamental aspects of basic quantum mechanics. It has been possible to study the decoherence (destruction of the inferred quantum entanglement) in different systems, even at ambient experimental conditions in condensed matter. Decoherence is now an important topic in quantum optics and related fields, but has been only recently considered in relation to condensed matter systems (see Refs. 6,37-39,51,53) and the special case of Bose-Einstein condensates.⁵⁴ It appears that quantum entanglement and its decoherence on the (sub)femtosecond level are much more ubiquitous phenomena in solid and liquid environments than thought before, especially when the lightest atoms are involved. They may have important consequences for various stages of many chemical reactions, including those of organic chemistry and molecular biology, and should therefore be given further attention.

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