High-Resolution Neutron Spectroscopy for the Investigation of Hydrogen Diffusion and Molecular Rotations in Solids*

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An introductory survey on applications of high-resolution neutron spectroscopy is presented, dealing with the motion of hydrogen in solids, namely concerning (i) random rotational motions or stationary tunneling states of NH$_4^+$-ions or CH$_4$-groups, and (ii) diffusion of hydrogen in alloys. For the rotation of hydrogenous groups in solids, at higher temperatures rotational jumps can be found, whereas quantum states are observed by μeV-spectroscopy at temperatures below 50 K. On the other hand, hydrogen diffusion does not reveal pronounced evidence of quantum effects, except for hydrogen in a metal containing impurity atoms.

**Key words**: Quasielastic neutron scattering; Diffusion; Tunneling.

1. Introduction

Neutron spectroscopy is a broadly applied research method in solid state physics, chemistry, polymer science, materials science, and biology. With respect to the methodical aspects, the activities cover two major fields: (i) The investigation of collective phenomena such as propagating excitations (phonons or magnons) and critical fluctuations; (ii) single-particle motions, which means in particular the rotation and the relaxation of molecular groups, and the diffusion of atoms in solids and liquids. The single-particle motion can be easily investigated for all dynamical processes where protons are involved, since, accidentally, the proton is a nucleus whose incoherent neutron scattering (i.e. scattering without coherency) is much stronger than the coherent scattering, which predominates for most of the nuclei. This incoherency is a consequence of the strong spin dependence of scattering, which is a property of the nuclear (n, p) interaction. The lecture note concentrates on the hydrogen motion and we will not deal with other nuclei, which also have some incoherent scattering contribution.

In the following we treat the study of (i) the rotation of ions, molecules or molecular groups, namely NH$_4^+$ or CH$_3$ in solids, and (ii) the diffusion of hydrogen atoms dissolved in metals and alloys. These investigations have in common an interesting basic aspect that is related to the small mass of the proton, which, under certain conditions, leads to quantum effects. We make a few general remarks on this subject in the summary paragraph. Details on neutron scattering in general and in these research fields can be found in many monographs [1–4], and we briefly explain the theoretical basis of the method, as well as a few experimental aspects, namely the μeV-backscattering spectroscopy, in Section 2. Then we present selected examples on molecular rotation and on diffusion of hydrogen in solids in Section 3. This includes mainly work from the Institut für Festkörperforschung, KFA Jülich.

2. Explanation of the Method

*Theory*

It can be easily derived (see the paper of K. Sturm in this Volume) that the incoherent scattering intensity on a sample is proportional to the incoherent cross-section per steradian dΩ, and per energy interval dE, namely

\[
d^2\sigma/d\Omega dE = a_{inc}^2 (E/E_0)^{1/2} S_{inc}(Q, \omega),
\]

where \(a_{inc}^2\) is the incoherent scattering length \(4\pi a_{inc}^2 = 79.7 \cdot 10^{-24} \text{ cm}^2\) for the hydrogen nucleus. The so-called dynamical structure factor \(S_{inc}(Q, \omega)\) is...
a function of energy transfer \( h\omega = E_0 - E_1 \), and of momentum transfer during scattering, \( hQ = h(k_0 - k_1) \), where \( E_0, E_1, k_0, \) and \( k_1 \) are the energies and wave vectors of the neutron before and after scattering, respectively. The dynamical structure factor can be expressed in terms of its Fourier transform in space (coordinate \( r \)) and in time (\( t \)) of the single-particle self-correlation function, as derived by van Hove [5], namely

\[
S_{\text{inc}}(Q, \omega) = (2\pi h)^{-1} \int \int G_s(r, t) e^{i(Qr-\omega t)} \, d^3r \, dt. \tag{2}
\]

This holds under the conditions of the first Fermi-Born approximation, which is very accurate in our case. \( G_s(r, t) \) is the self-correlation function of the scattering proton, such that \( G_s(r, t) \, d^3r \) describes the probability to find a moving particle (the proton) at a position \( r \) for a time \( t \), if it has been at a position \( r = 0 \) for a previous time \( t = 0 \).

Figure 1 presents \( G_s(r, t) \) for a diffusing particle as it can be calculated in the so-called Chudley-Elliott theory [6]. It starts, for \( t = 0 \), in the origin; after a certain time there is a finite probability to find it distributed over a number of sites of the lattice. The corresponding Fourier transform \( S_{\text{inc}}(Q, \omega) \) is shown schematically in Figure 2. It is a Lorentzian centered at \( h\omega = 0 \) ("quasielastic line") whose width \( \Gamma(Q) \) increases with \( Q \) as

\[
\Gamma = Q^2 D_s \quad \text{for} \quad (Q l)^2 \ll 1, \tag{3}
\]

where \( D_s \) is the self-diffusion coefficient of the particle (Figure 2). For large \( Q \), the width \( \Gamma(Q) \) changes its curvature; in the maximum, \( \Gamma(Q) \) is a function of the vectors \( l \) connecting the interstitial lattice points over which the diffusive steps occur, and to the jump rate \( 1/\tau \), where \( \tau \) is the average rest time of the proton on an interstitial site. The time for the jump itself (\( \approx 10^{-13} \) s) can be normally neglected. Thus, in general, a quasielastic scattering (QES) experiment on crystals with hydrogen yields the self-diffusion coefficient \( D_s \) and, in addition, geometrical details of the diffusive jump mechanism, in particular, if the experiments are carried out on a single crystal. \( D_s \) is the quantity which could also be measured "macroscopically", e.g. by tracer methods, or field-gradient nmr. For QES, the proton is labelled by its nuclear spin.

On the other hand, for rotations of a molecular group about an axis, the self-correlation function looks schematically as shown in Figs. 3 a and b, which present \( G_s(r, t) \) dependent on time \( t \). It indicates the probability of occupancy for a rest site, where a fourfold rotation of a single proton, e.g. in an NH\(_4\)-ion, is assumed. The probability of occupancy decays with a certain relaxation time. For \( t \to \infty \), the self-correlation function approaches a finite value, namely

\[
G_s(r, \infty) = G_{\infty}(r),
\]

since the hydrogen atom has a finite
probability to be somewhere. $G_\infty(r)$ is the asymptotic distribution after a sufficiently large number of rotational jumps has occurred, whereas for the translational diffusion $G_\infty$ approaches zero since the particle is distributed over the practically infinite volume of the whole sample. The corresponding $S_{\text{inc}}(Q, t)$ for rotation is again a Lorentzian curve as in Fig. 2, whose width is related to $1/\tau_\text{r}$, the average rate of rotational jumps. However, owing to the finite $G_\infty$, a sharp peak (or delta function) is superimposed at $\omega = 0$, as shown in Fig. 3c. Its intensity is proportional to the Fourier transform of $G_\infty(r)$ in space. This line can be understood as the diffraction of the neutron wave by a single proton, which is distributed over a finite but restricted volume in space by the rotational jumps [7]. So we have

$$S_{\text{inc}}(Q) = \int e^{iQr} G_\infty(r) \, d^3r,$$

where $S_{\text{inc}}(Q)$ is the elastic incoherent structure factor, normally called EISF. It must be distinguished from the coherent structure factor due to waves scattered coherently from different nuclei.

So far, these considerations were based on classical proton motions. This holds as long as $t \geq h/kT$. Typically, this criterion is fulfilled at temperatures above, say, 100 K and for times larger than $10^{-12}$ sec. On the other hand, quantum mechanics dominates at low temperatures, this means for the tunneling excitations which are described later. In this latter case the dynamical structure factor has to be calculated from transition matrix elements for the (stationary) wave functions of the proton. Also the EISF changes its sense since the elastic processes are then correlated with the protonic spins [8]. To summarize, the investigation of the quasielastic line and the EISF tells us about the sites (or paths) over which the proton moves, and it yields the corresponding time(s) or rate(s). For rotation at low temperature, we get the energy states of the rotator wave functions, and, from the EISF, under certain conditions the protonic wave functions.

On the Experimental Methods

The spectrum or the width $I(Q)$ for quasielastic scattering, or the transition energies for tunneling, are normally found between 0.1 and $10^{-7}$ eV. The range above $10^{-4}$ eV is covered by time-of-flight methods which we will not describe. For energy transfers $h\omega$ in the region of a few $10^{-5}$ to $10^{-7}$ eV the so-called backscattering method is being used [9].

In this method, the energies before and after scattering, $E_0$ and $E_1$, are selected by Bragg reflection on an ideal silicon single crystal under 90° angle. It is well-known that the relation between neutron wave length $\lambda$ and the Bragg angle $\phi_B$ is given by the Bragg law, namely $\lambda = 2d_{hkl} \sin \phi_B$, where $d_{hkl}$ is the lattice distance for a certain set of planes. Obviously, if $\phi_B$ approaches 90°, the beam divergency (i.e. the width of $\phi_B$) enters only in second order, so its contribution to the resolution width $\Delta E$ or $\Delta h\omega$ is rather small. The main contribution of the energy resolution is then due to the Darwin width, which is determined by extinction in the crystal; it is given by $\Delta E/E = 32\pi NF/G^2_{hkl}$ where $N$ is the unit cell density and $G_{hkl}$ is the reciprocal lattice vector of the crystal. $F$ is the structure factor. The resulting energy resolution of a spectrometer working on this basis is 0.2–2 $\mu$eV (see [10]).

3. Rotation of Molecular Groups in Solids

Two experiments on the rotation of hydrogenous groups will be presented; the first is exemplary for the high-temperature behaviour of rotational jumps of the ammonium group in NH$_4$Cl [11]. Secondly, we refer to a very detailed investigation of CH$_3$-group tunneling in dimethylbenzene at low temperatures [12]. In this case, so-called tunneling spectra in the $\mu$eV range were observed and studied.

Rotational Jumps of NH$_4^+$ in Ammonium Chloride

QES experiments were carried out on NH$_4$Cl with the Jülich backscattering spectrometer, using a single-crystalline NH$_4$Cl sample [11]. By choosing different orientations of the scattering vector $Q$ relative to the crystal axis, it was possible to separate and identify the elastic-line intensity (the EISF in Eq. (4)) and the superimposed quasielastic contributions for the different kinds of rotation. The results were interpreted in terms of 90° rotational jumps about <100> axes, i.e. between different orientations of the NH$_4$-group ($\sigma = 1$ and $\sigma = -1$, see Fig. 4), and rotations that interchange only the H-positions of the NH$_4^-$-ion, but leave its orientation unchanged; this motion could be understood by a 120° rotation about a $\langle 111 \rangle$ axis. The corresponding rotational jump rates are called $v_4$ and $v_3$. 
termined. For the fourfold jumps they agree quite well with calculations on the basis of combined NH$_4^+$ octupole–octupole, and NH$_4^+$ octupole–Cl$^-$-ion interactions. The first one practically disappears in the disordered phase. For $v_3$, the obtained activation energy does not agree. This is assumed to be due to the fact (and confirmed by calculations), that, for the $v_3$-jumps, the molecule actually does not rotate about a fixed $\langle 111 \rangle$ axis; rather the axis of rotation is tumbling, thus avoiding the high potential barrier between the equilibrium orientations. The investigation of the way how the molecule rotates is an interesting problem for plastic crystals in general and it would be worth investigating also for other cases.

**Stationary Rotational Tunneling States of Methyl Groups in an Organic Crystal**

With the availability of the $\mu$eV backscattering spectroscopy numerous experiments were performed on CH$_3$-compounds, as well as on other solids with hydrogenous groups at low temperatures, say $< 40$ K [8]. In this region rotational jumps are extremely slow and the quasielastic component practically disappears in the spectra. Instead, the spectra exhibit several sharp lines near the elastic line in the $\mu$eV region. Figure 6 shows a typical spectrum in the $\mu$eV range for a methyl compound [14]. A single transition is observed on the energy-loss and the energy-gain side, with the elastic line in the center. These two “tunneling lines” are due to up- and down-transitions between stationary quantum states for the three protons of the CH$_3$-group, which are exposed to the three or sixfold angular-dependent hindrance potential around the rotational axis (see [13]). Figure 7 shows schematically (for a purely sixfold potential) how we can imagine the concentration of the overlapping wave functions in the “potential pockets”. In addition to these so-called tunneling transitions, there are also spectral lines at much higher energy in the $10^{-3}$ to $10^{-2}$ eV region caused by transitions between the (tunneling-splitted) librational states of such a group.

A recent collaboration with a research group in the Rutherford Appleton Laboratory in Oxford dealt with an analysis of such tunneling and librational spectra, which were determined and used to explore the rotational potential $V(\phi)$ [12]. The potential was calculated by means of different 6–12 or 6–exponential pair potentials $V(r_{ij})$, which act between the three hydrogen atoms (i) of the CH$_3$-group and the sur-
Fig. 6. Typical tunneling spectrum with lines on the energy-loss and gain side for a CH$_3$-group in (CH$_3$)$_2$C$_2$ as measured by backscattering spectroscopy [14].

rounding C and H atoms ($j$), where $r_{ij}$ depends on the rotation angle $\phi$ of the CH$_3$-group, such that

$$V(\phi) = \sum_{i=1}^{3} \sum_{all j} V[r_{ij}(\phi)].$$

(5)

The sum goes over all mutual C–H and H–H contributions. From this potential the Schrödinger equation and its eigenvalues were calculated, and hence the tunneling and librational transition energies. However, the comparison with their experimental values was not satisfactory, i.e. the chosen potential functions are partly insufficient. So, nevertheless, we can conclude that this work is a careful and exemplary demonstration what accuracy could be obtained on certain features of the interaction potential in molecular crystals.

Numerous experiments were carried out in this field. The aim of the studies is either an investigation of the potentials as described above, its pressure dependence [15], or the local symmetry of CH$_3$-groups [16]. In addition, it was tried to discover the effect of coupling between CH$_3$-groups [17]. An interesting problem is the time dependence of such spectra, because a tunneling state is related to a spin state (or to certain spin states), and spin conversion occurs [18].

4. Hydrogen Diffusion in Metals and Alloys

Quasielastic scattering experiments were carried out with simple hydrides, in particular on fcc Pd and on bcc Nb, Ta, and V, having octahedral or tetrahedral interstitial sites occupied by hydrogen atoms, respectively. These experiments served in particular to evaluate the details of the jump mechanisms (for detailed reviews see [19, 20]). One of our results on the bcc hydrides was that, e.g. for hydrogen in Nb, one observes correlated jump sequences. They are caused by the following process: A hydrogen atom on an interstitial site creates a strong distortion field, which lowers the hindrance barriers between interstitial sites. The decay of the strain field is relatively slow, which causes preferential jumps between adjacent sites passing over these lowered barriers. The experiments have demonstrated that fast sequences of three or more jumps can occur until the proton finally “falls” into a site where the rest time is much longer than in the unrelaxed sites. Many experiments have also been carried out in order to investigate the self diffusion constant, by extrapolating the quasielastic widths to small $Q$-values (see (3)) [21]. For storage hydrides this method turned out to be more reliable than others.
Recent experiments in our laboratory dealt with \( \text{LaNi}_5 \text{H}_x \) \cite{22}, whose lattice cell is shown in Figure 8. A single crystal with the \( ^{60}\text{Ni} \) isotope was available (in order to reduce parasitic incoherent scattering). Figure 9 presents typical quasielastic spectra for the diffusing hydrogen. From the interpretation of quasielastic-scattering spectra for different orientations for the scattering vector \( \mathbf{Q} \) (using an extension of the Chudley-Elliott theory \cite{6}), three types of jumps had to be postulated: jumps in the basal plane of the hexagonal lattice, and jumps between the lower and the middle basal planes in the \( c \)-direction (Figure 8). This mechanism shows up by quasielastic lines that have a width of the order of \( 1 \mu\text{eV} \) or less, corresponding to jump rates at \( 423 \text{ K} \) of \( 2 \cdot 10^8 \text{ s}^{-1} \) (in the basal plane \( 3f \rightarrow 3f \)), and \( 2 \cdot 10^9 \text{ s}^{-1} \) (between basal planes \( 6m \rightarrow 3f \)), depending on temperature with an Arrhenius law. Surprisingly, in addition a very broad quasielastic line was observed for \( \mathbf{Q} \) perpendicular to the \( c \)-axis, whose width is about 200 times larger than the width for the jumps mentioned before. The corresponding motion is attributed to a process where the hydrogen rocks around a \( c \)-axis near the lanthanum atoms as indicated in the figure, with a jump rate of roughly \( 10^{11} \text{ s}^{-1} \). Such a fast “local” jump motion, which does not contribute to the diffusive transport, was also found in the QES spectra of another storage alloy, namely \( \text{TiMn}_2 \) loaded with hydrogen \cite{23}.

In the hydrogen diffusion process, quantum effects could not be identified in the QES spectra. However, neutron scattering on \( \text{NbH}_x \) doped with a few 0.1\% of nitrogen at very low temperatures, where diffusion is practically frozen, revealed a clear doublet near the elastic line, as observed by a group in Darmstadt \cite{24}. This doublet was attributed to transitions for the quantum states of a hydrogen “smeared” between two adjacent tetrahedral sites in the close vicinity of an octahedral interstitial impurity. This interpretation is supported by experiments on the specific heat which show an anomalous contribution at rather low temperature with a very strong isotope effect. Such “local quantum states” were also observed at low temperatures for hydrogen in \( \text{Nb} \), doped with \( \text{Ti} \) atoms at low temperatures. Also here broad lines on the energy-loss and gain side are visible in the neutron spectra with energies of about \( 10^{-4} \text{ eV} \) \cite{25}. The details of these excitations of an \( \text{H} \) trapped near \( \text{Ti} \) impurities are not yet clear.

Recent quasielastic scattering experiments for hydrogen in fcc scandium yielded the usual QES spectra caused by diffusion. However, at low temperatures (<50 K) a broadening persisted, which cannot be attributed to diffusion \cite{26}. It could be understood in terms of a “local quantum motion” of the hydrogen, similar to the effect described before.
Energy Transfer (μeV)

Fig. 9. Typical quasielastic spectra for hydrogen diffusion in α-LaNi₅ hydride (the narrow part only). $h\omega$ is the energy transfer. Dashed: resolution curve (from [22]).

5. Résumé, Quantum Effects or Not?

We have presented examples that show what kind of information we extract from neutron spectroscopy on the hydrogen motion, being of classical nature or governed by quantum mechanics. For the molecular rotations in a solid we have shown (Sect. 3) that transitions appear in the μeV region between levels of the stationary ground state of molecular librations around an axis, which are splitted by the overlap of wave functions in the periodic hindrance potential. The existence of such transitions was already predicted a long time ago from $1/T_1$ vs. temperature-curves that loose their conventional V-shape under such conditions (see [27]); these transitions were directly observed by the μeV neutron spectroscopy for the first time. With increasing temperature, the phonons modulate the phase and the amplitude of the hindrance potential acting on the molecular groups. This, first, leads to an interaction between tunneling states and single phonons, thus inducing a shift of the transition energies [28]. With increasing temperature, however, the phonon fluctuations destroy the stationary quantum states entirely, which finally leads to the randomized “rotational jumps” as described before. The very complex phenomenon of a quantum state that couples to a bath of thermally excited phonons was studied for this situation [29]. On the other hand, no pronounced quantum effects were found for hydrogen diffusion in metals. At least, we can say that quasielastic scattering does not indicate any delocalization of the proton wave function; but there is an isotope effect (going from hydrogen to deuterium or tritium) for the temperature dependence of the self-diffusion constant. The hydrogen localization is due to the strong elastic distortion field (“elastic polaron”) that a hydrogen creates in the host lattice [30]; this distortion moves with the hydrogen during diffusion such that, in a sense, the “effective mass” is very large, and there is practically no energy band for this protonic motion. At low temperatures, a hydrogen finally precipitates in stable superstructures, which leads to a still stronger
binding of the hydrogen on its sites. Nevertheless, tunneling transitions were observed by neutron spectroscopy under special conditions, namely for hydrogen in metals with impurities. This means that hydrogen atoms are trapped, e.g. on an interstitial, or on a substitutional atom, and that this localization leads to a stationary quantum state as described in Section 4. Let us finish with an aspect that leads away from the experiments described so far. The muon has $1/9$ of the proton mass and is thus a very light hydrogen isotope (only the positron is even lighter). As a consequence, very large quantum effects exist for muon diffusion, as measured by resonance spectroscopy \[31\]. As usual, the observed diffusion constant first decreases with decreasing temperature. However, below $5 \text{ K}$ the diffusion constant or hopping rate starts to increase again if the temperature decreases. This means: For high temperatures, muon diffusion is promoted by the thermal motion of the host lattice. At low temperatures, however, there seems to be delocalization of the muon wave function. This enhances the mobility, but the thermal motion hinders the diffusive step, thus leading to the observed inverse temperature dependence.

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