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

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Z. Naturforsch. **48a,** 406–414 (1993); received January 7, 1992

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_3-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 d*E*, namely

$$d^2\sigma / d\Omega \, dE = a_{\text{inc}}^2 (E_1/E_0)^{1/2} \, S_{\text{inc}}(\boldsymbol{Q}, \omega) , \qquad (1)$$

where a_{inc} is the incoherent scattering length ($4\pi a_{\text{inc}}^2 = \sigma_{\text{inc}} = 79.7 \cdot 10^{-24}\ \text{cm}^2$ for the hydrogen nucleus). The so-called dynamical structure factor $S_{\text{inc}}(\boldsymbol{Q}, \omega)$ is

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* Presented at the Sagamore X Conference on Charge, Spin and Momentum Densities, Konstanz, Fed. Rep. of Germany, September 1–7, 1991.

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a function of energy transfer $\hbar\omega = E_0 - E_1$, and of momentum transfer during scattering, $\hbar \boldsymbol{Q} = \hbar(\boldsymbol{k}_0 - \boldsymbol{k}_1)$, where E_0, E_1, $\boldsymbol{k}_0$, and $\boldsymbol{k}_1$ 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 $\boldsymbol{r}$) and in time (t) of the single-particle correlation function, as derived by van Hove [5], namely

$$S_{\text{inc}}(\boldsymbol{Q}, \omega) = (2\pi\hbar)^{-1} \iint G_s(\boldsymbol{r}, t)\, e^{i(\boldsymbol{Q}\boldsymbol{r} - \omega t)}\, \mathrm{d}^3\boldsymbol{r}\, \mathrm{d}t\,. \quad (2)$$

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

Figure 1 presents $G_s(\boldsymbol{r}, t)$ 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 $S_{\text{inc}}(\boldsymbol{Q}, \omega)$ is shown schematically in Figure 2. It is a Lorentzian centered at $\hbar\omega = 0$ ("*quasielastic line*") whose width $\Gamma(\boldsymbol{Q})$ increases with Q as

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

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 $\boldsymbol{l}$ connecting the interstitial lattice points over which the diffusive steps occur, and to the jump rate $1/\tau$, where τ is the average rest time of the proton on an interstitial site. The time for the jump itself ($\simeq 10^{-13}$ 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.

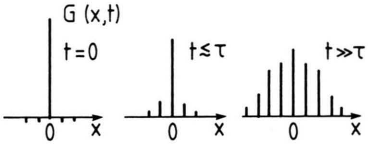

Fig. 1. The self-correlation function $G_s(x, t)$ (schematic in one dimension) for an atom on a lattice, with increasing time t.

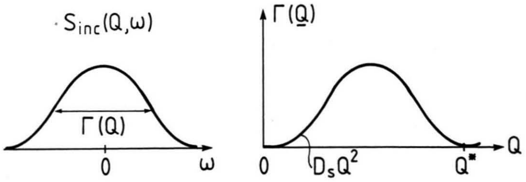

Fig. 2. Incoherent dynamical structure factor for a hydrogen atom diffusing in a lattice, $S_{\text{inc}}(\boldsymbol{Q}, \omega)$, as a function of energy transfer $\hbar\omega$ and length Q of the scattering vector $\boldsymbol{Q}$, and the quasielastic width $\Gamma(Q)$. The curvature at small Q yields the self-diffusion constant D_s, the value in the maximum is proportional to $1/\tau$ (mean rest time). Q^* is a reciprocal lattice vector of the interstitial lattice where $\Gamma = 0$.

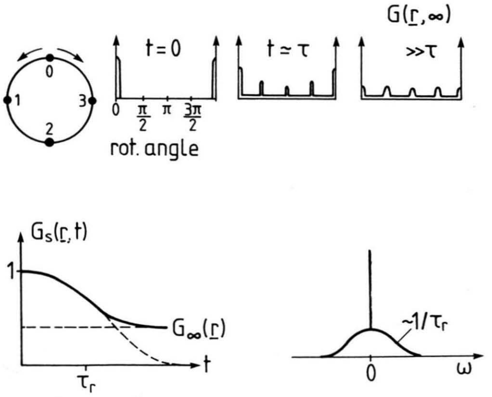

Fig. 3. (a) Self-correlation function $G_s(\boldsymbol{r}, t)$ for a hydrogen atom, e.g. in an NH_4^+-ion, rotating around a [100] axis with four rest positions for different times t. (b) $G_s(\boldsymbol{r}, t)$ for a given position as a function of time. For the rotating group, G_s approaches a finite value $G_\infty(\boldsymbol{r})$. For a freely diffusing atom (dashed) $G_s(\boldsymbol{r}, t)$ goes to zero for $t \to \infty$. (c) $S_{\text{inc}}(\boldsymbol{Q}, \omega)$ for a rotating molecule. The elastic line (at $\omega = 0$) is superimposed on the quasielastic line. τ_r is the characteristic time of the rotation.

On the other hand, for *rotations of a molecular group* about an axis, the self-correlation function looks schematically as shown in Figs. 3a and b, which present $G_s(\boldsymbol{r}, t)$ 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 $G_s(\boldsymbol{r}, \infty) = G_\infty(\boldsymbol{r})$, since the hydrogen atom has a finite probability to be *somewhere*. $G_\infty(\boldsymbol{r})$ is the asymptotic distribution after a sufficiently great number of rotational jumps has occurred, whereas for the translational diffusion G_∞ approaches zero since the particle is distributed over the practically infinite volume of the whole sample. The corresponding $S_{\text{inc}}(\boldsymbol{Q}, t)$ for rotation is again a Lorentzian curve as in Fig. 2, whose width is related to $1/\tau_r$, the average rate of rotational jumps. However, owing to the finite G_∞ 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 $G_\infty(\boldsymbol{r})$ 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

$$S_{\text{inc}}(\boldsymbol{Q}) = \int e^{i\boldsymbol{Q}\boldsymbol{r}}\, G_\infty(\boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r}\,, \tag{4}$$

whrere $S_{\text{inc}}(\boldsymbol{Q})$ 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 $t \gtrsim \hbar/kT$. Typically, this criterium 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 $\Gamma(\boldsymbol{Q})$ 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 $\hbar\omega$ 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 λ and the Bragg angle ϕ_{B} is given by the Bragg law, namely $\lambda = 2\,d_{hkl}\sin\phi_{\text{B}}$, where d_{hkl} is the lattice distance for a certain set of planes. Obviously, if ϕ_{B} approaches 90°, the beam divergency (i.e. the width of ϕ_{B}) enters only in *second order*, so its contribution to the resolution width ΔE or $\Delta\hbar\omega$ 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 $\Delta E/E = 32\pi NF/G_{hkl}^2$ where N is the unit cell density and $\boldsymbol{G}_{hkl}$ 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 μeV (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_4Cl [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 μeV range were observed and studied.

Rotational Jumps of NH_4^+ in Ammonium Chloride

QES experiments were carried out on NH_4Cl with the Jülich backscattering spectrometer, using a single-crystalline NH_4Cl sample [11]. By choosing different orientations of the scattering vector $\boldsymbol{Q}$ 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 $\langle 100 \rangle$ 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 ν_4 and ν_3.

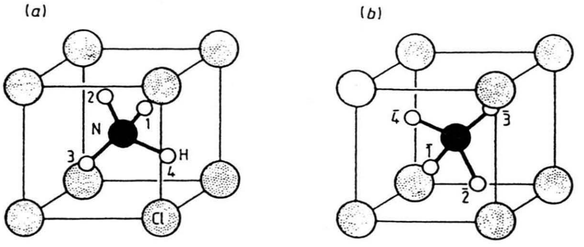

Fig. 4. Orientation of an NH_4^+-ion in the NH_4Cl lattice. (a) and (b) correspond to the two possible orientations $\sigma = \pm 1$. Below the phase transition all tetrahedra occupy one orientation, above the phase transition the orientation is random.

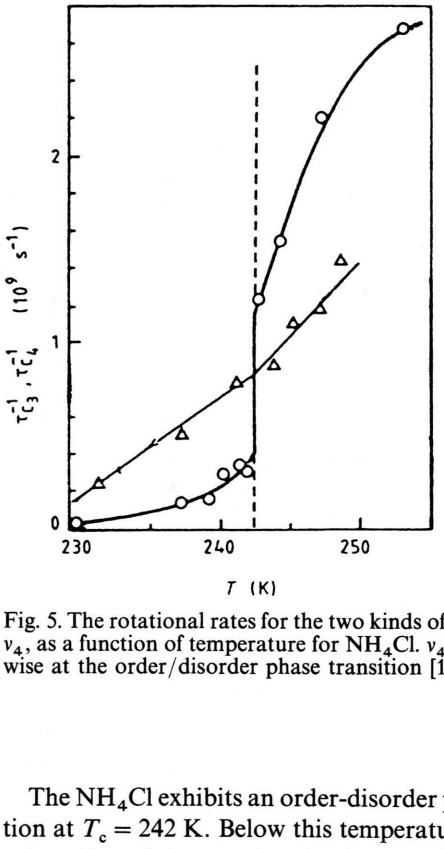

Fig. 5. The rotational rates for the two kinds of jumps, ν_3 and ν_4, as a function of temperature for NH_4Cl. ν_4 changes stepwise at the order/disorder phase transition [11].

The NH_4Cl exhibits an order-disorder phase transition at $T_c = 242$ K. Below this temperature, the ionic orientations (σ) are ordered, whereas above T_c they are at random. Figure 5 presents the obtained rotational rates ν_4 and ν_3 vs. temperature. Obviously, ν_4 changes abruptly at T_c, due to the change of the molecular field, which depends on the (average) NH_4^+-orientations; on the other hand, ν_3 goes smoothly through this transition. From these experiments, the activation energies for the rotational jumps were determined. 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 ν_3, the obtained activation energy does not agree. This is assumed to be due to the fact (and confirmed by calculations), that, for the ν_3-jumps, the molecule actually does not rotate about a fixed ⟨111⟩ 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 μeV 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 μeV region. Figure 6 shows a typical spectrum in the μeV 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-

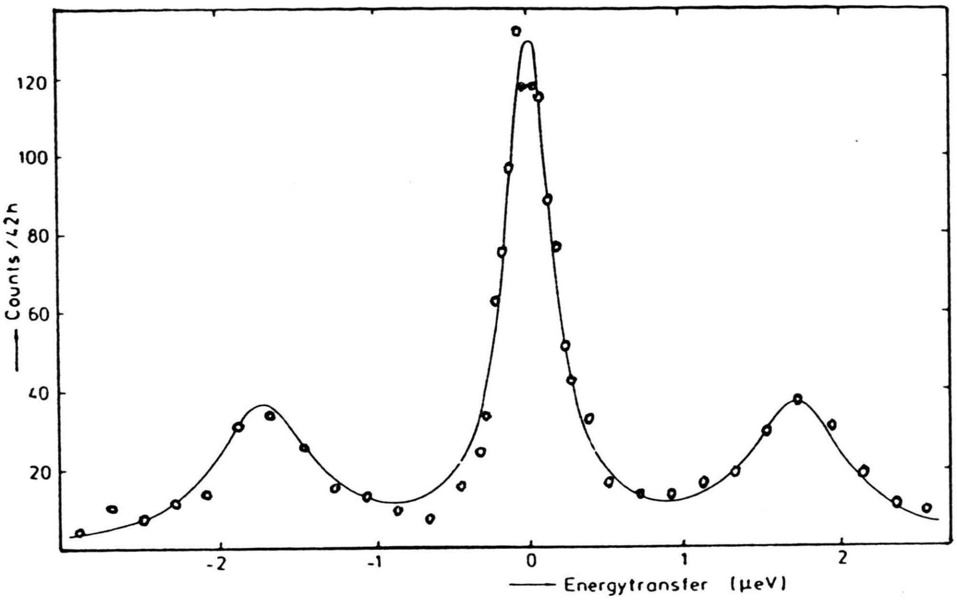

Fig. 6. Typical tunneling spectrum with lines on the energy-loss and gain side for a CH_3-group in $(CH_3)_2C_2$ as measured by backscattering spectroscopy [14].

rounding C and H atoms (j), where r_{ij} depends on the rotation angle ϕ of the CH_3-group, such that

$$V(\phi) = \sum_{i=1}^{3} \sum_{\text{all } j} V[r_{ij}(\phi)] . \tag{5}$$

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.

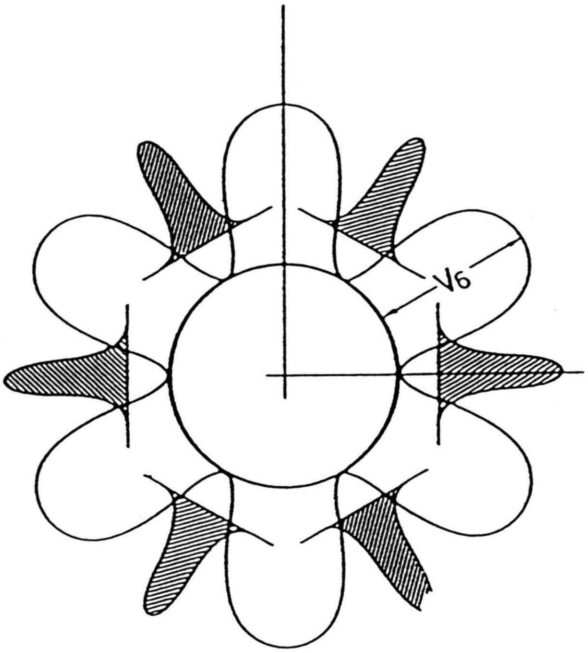

Fig. 7. Periodic potential V_6 with the wave function of a single proton (shaded), showing the "pocket states" (from [8(a)]).

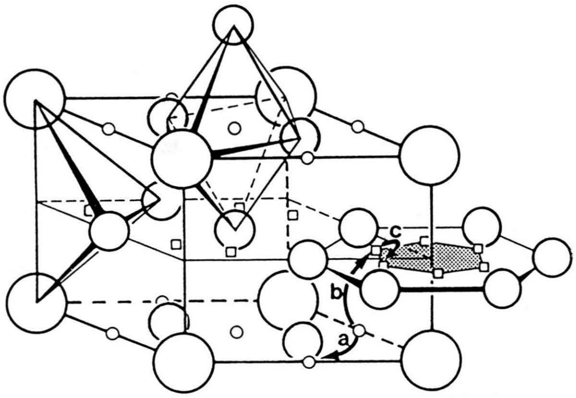

Fig. 8. Lattice cell of $LaNi_5$-hydride indicating the interstitial hydrogen sites. Large circles: Ni, small circles: La. o, □ denote possible hydrogen sites. The diffusion is supposed to follow jumps between the basal planes; a very rapid motion occurs around the *c*-axis (shaded). o = 3 f, □ = 6 m sites.

Recent experiments in our laboratory dealt with $LaNi_5H_x$ [22], whose lattice cell is shown in Figure 8. A single crystal with the ^{60}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 quasi-elastic-scattering spectra for different orientations for the scattering vector $\boldsymbol{Q}$ (using an extension of the Chudley-Elliott theory [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 μeV or less, corresponding to jump rates at 423 K of $2 \cdot 10^8\ s^{-1}$ (in the basal plane $3f \rightarrow 3f$), and $2 \cdot 10^9\ s^{-1}$ (between basal planes $6m \rightarrow 3f$), depending on temperature with an Arrhenius law. Surprisingly, in addition a very broad quasi-elastic line was observed for $\boldsymbol{Q}$ 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 $10^{11}\ s^{-1}$. 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 $TiMn_2$ loaded with hydrogen [23].

In the hydrogen diffusion process, quantum effects could not be identified in the QES spectra. However, neutron scattering on 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 [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 Nb, doped with 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} eV [25]. The details of these excitations of an H trapped near 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 [26]. It could be understood in terms of a "local quantum motion" of the hydrogen, similar to the effect described before.

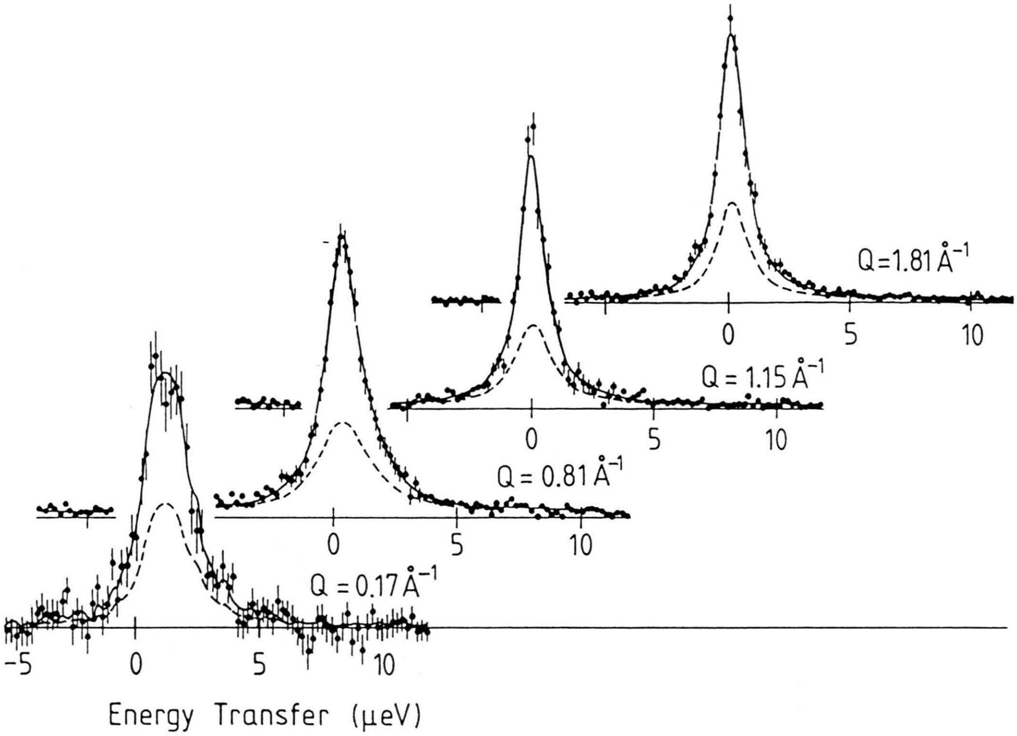

Fig. 9. Typical quasielastic spectra for hydrogen diffusion in α-LaNi$_5$ hydride (the narrow part only). $\hbar\omega$ is the energy transfer. Dashed: resolution curve (from [22]).

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 K the diffusion constant or hopping rate startes 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.

Acknowledgement

The author is grateful for stimulating discussions with Dr. Rolf Hempelmann and Dr. Michael Prager, and to Marlene Kraus for preparing the manuscript.

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