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Quasi-elastic Scattering of Neutrons for the Study of Random Motions in Solids

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(Z. Naturforsch. **26 a**, 575—584 [1971]; received 30 November 1970)

Dedicated to Prof. Dr. H. Maier-Leibnitz on his 60th birthday

Investigations on motions of hydrogen atoms in metals, on rotational diffusion in molecular solids and on fluctuations of protons at hydrogen bonds are reviewed as examples for experiments with incoherent neutron scattering requiring high resolution.

1. Introduction

In solids random motions of atoms may take place in connection with disorder; for instance diffusion of interstitials in solid solutions or orientation fluctuations in molecular solids. Experimentally these motions are observed mostly by resonance and relaxation techniques, by optical spectroscopy and, recently, by neutron spectroscopy. In comparison to the other methods neutron spectroscopy has the advantage, that it permits an observation of these motions not only in time but also in space.

Moreover, as neutron scattering can be described in first Born approximation[1], the evaluation of experimental data is comparatively simple. The intensity of neutrons scattered into solid angle $d\Omega$ and into an energy interval dE is proportional to the differential cross-section[2]

$$\frac{d\sigma}{d\Omega\, dE} = \frac{1}{\hbar}\,\frac{k}{k_0}\,\frac{1}{4\pi}\,[\sigma_{\text{inc}}\, S_{\text{inc}}(\boldsymbol{\varkappa}\,,\omega) + \sigma_{\text{coh}}\, S_{\text{coh}}(\boldsymbol{\varkappa}\,,\omega)]\,, \tag{1}$$

where $\hbar\,\boldsymbol{\varkappa} = \hbar\,(\boldsymbol{k}_0 - \boldsymbol{k})$

and $\hbar\,\omega = E_0 - E = \dfrac{\hbar^2}{2\,m}\,(k_0{}^2 - k^2)$

are the momentum and energy transfer during the scattering process, $\boldsymbol{k}_0$, $\boldsymbol{k}$, E_0 and E are the wave vector and the energy of the incident and scattered neutrons, respectively. The scattering cross-section (1) is factorized into terms which depend on the interaction of the neutron with the nuclei, and functions determined only by the properties of the scattering system, namely

$$S_{\text{inc}}(\boldsymbol{\varkappa}\,,\omega) = \frac{1}{2\,\pi}\int G_{\text{s}}(\boldsymbol{r},t)\,\exp\{i(\boldsymbol{\varkappa}\boldsymbol{r} - \omega\,t)\}\,d\boldsymbol{r}\,dt\,,$$

$$S_{\text{coh}}(\boldsymbol{\varkappa}\,,\omega) = \frac{1}{2\,\pi}\int [G_{\text{s}}(\boldsymbol{r},t) + G_{\text{d}}(\boldsymbol{r},t)] \cdot \exp\{i(\boldsymbol{\varkappa}\boldsymbol{r} - \omega\,t)\}\,d\boldsymbol{r}\,dt\,. \tag{2}$$

Here in a classical approximation $G_{\text{s}}(\boldsymbol{r}-\boldsymbol{r}_0\,, t-t_0)\,d\boldsymbol{r}$ is the probabality that a nucleus, which at time t_0 was at $\boldsymbol{r}_0$ will be in volume element $d\,\boldsymbol{r}$ at $\boldsymbol{r}$ at time t, and $G_{\text{d}}(\boldsymbol{r}-\boldsymbol{r}_0\,, t-t_0)\,d\,\boldsymbol{r}$ the probability that there will be a nucleus at time t at $\boldsymbol{r}$, if at time t_0 a different nucleus has been at $\boldsymbol{r}_0$. G_{s} is called the self-correlation function, G_{d} the time-dependent pair correlation function, $G = G_{\text{s}} + G_{\text{d}}$ is the general Van Hove correlation function. The scattering process can be visualized as a Fourier analysis of these correlation functions in space and time. In Fig. 1 the $\boldsymbol{\varkappa}$- and ω-regions accessible to neutrons are compared to regions accessible with other methods. The use of large $\varkappa$-values permits the observation of particle motions over small distances.

The interaction of the neutron with the nuclei is described by the quantities σ_{inc}, which is the bound nucleus cross-section for incoherent scattering, and σ_{coh} the one for coherent scattering;

$$\sigma_{\text{inc}} = 4\,\pi\,(\langle a^2\rangle - \langle a\rangle^2)\,, \qquad \sigma_{\text{coh}} = 4\,\pi\langle a\rangle^2,$$

$$\langle a^2\rangle = \frac{1}{N}\sum_{\nu} N_\nu\, a_\nu{}^2, \qquad \langle a\rangle^2 = \frac{1}{N^2}\,(\sum_{\nu} N_\nu\, a_\nu)^2,$$

if a_ν is the scattering amplitude, N_ν the number of nuclei of kind ν with $\sum_{\nu} N_\nu = N$.

The disadvantage of neutron spectroscopy lies in the small primary intensity available from research reactors. Much effort has been spent in recent years to increase the primary intensity (high flux reactors) and to develop instruments of higher resolution which will utilize the available intensity in an optimal way. In this connection a new type of spectrometer is to be mentioned. It originated from a proposal of Maier-Leibnitz and for the first time has been built and operated at

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[1] See V. TURCHIN, Slow Neutrons, Israel Program for Sci. Transl. 1965.

[2] L. VAN HOVE, Phys. Rev. **95**, 249 [1954].

the FRM reactor in Munich. The energy resolution of a Bragg monochromator is given by

$$\delta E/E \cong 2\,|\operatorname{ctg}\Theta\cdot\delta\Theta\,|+2\,|\,\delta G/G\,|$$

where Θ is the Bragg angle, $\delta\Theta$ is its uncertainty due to mosaic spread and beam divergence, $\delta G/G$ (G = reciprocal lattice vector) is the resolution width due to extinction, which means that only a finite number of lattice planes are illuminated by the incident beam. In a typical case, $\delta G/G \cong 10^{-4}$. Therefore, if Θ is about 90°, $\delta E/E$ is to first order only given by the last term even if a beam with a relatively wide angular spread is used. The resolution width achieved with such an instrument, where $\Theta = 90°$ for both, the monochromizing and analyzing crystal, is of the order[3] of

$$\delta E \cong 5\cdot 10^{-7}\ \text{eV}.$$

The energy E_0 is varied by a Doppler motion of the Bragg crystal. By the existence of this new type of instrument, the ω-range which can be covered by neutrons (Fig. 1) overlaps now with the typical frequencies of NMR, acoustic and electric relaxation methods. This region is of special importance for problems concerning the random or quasi-random atomic motions in solids which are very slow in many cases.

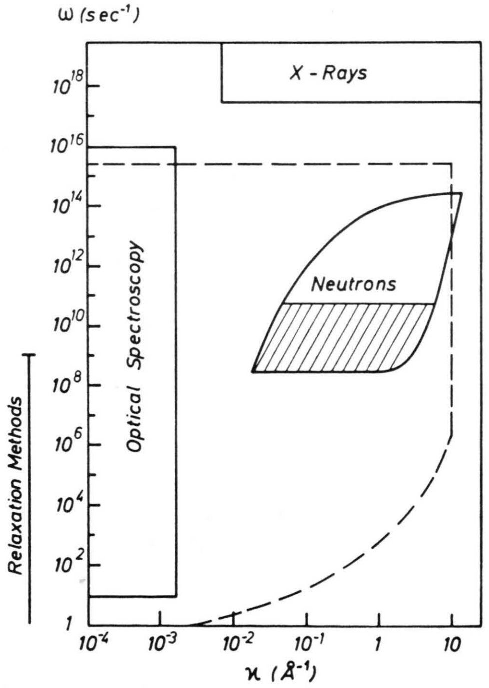

Fig. 1. The $\varkappa$-ω-regions accessible with different experimental techniques. The shaded part of the neutron region indicates the part which has become accessible for certain investigations with the new spectrometer described in the introduction. The dashed contour indicates the region of interest in dynamical problems in solid and liquid state physics and for physical chemistry.

In the following we give a review on several problems related to such motions, with special emphasis on the work carried out at our laboratory. We limit the discussion to the so-called "quasi-elastic" region, where the effects of slow random motions are dominating. If the scattering nuclei perform harmonic oscillatory motions only, the incoherent scattering law $S_{\text{inc}}(\boldsymbol{\varkappa},\omega)$ is composed of a sharp line at $\omega = 0$ ("Mössbauer-line") and a distribution of intensity at larger ω corresponding to energy loss or gain of the neutrons by excitation or deexcitation of the vibrational motions. If, in addition to the vibrations, the nuclei also perform random motions, for instance between the interstitial sites of a crystal, then the elastic line or a part of it become broadened. A broadened elastic line is called quasi-elastic. Its intensity, its width and its shape, measured as a function of $\boldsymbol{\varkappa}$, yield information on the random motions in space and time.

2. Hydrogen Motion in Metals

Hydrogen can be dissolved in many metals up to very high concentrations. The protons occupy interstitial positions of the lattice and are able to perform a diffusive motion which could be described by jumps between these interstitial sites. A theory has been worked out by CHUDLEY and ELLIOTT[4] to calculate the scattering law for such diffusing protons: The time-dependent probability $P(\boldsymbol{r},t)$ of finding a particle at $\boldsymbol{r}$, should follow a rate equation, namely:

$$\frac{\partial P(\boldsymbol{r},t)}{\partial t} = \frac{1}{n\,\tau}\sum_{\boldsymbol{s}_j}\left[P(\boldsymbol{r}+\boldsymbol{s}_j,t)-P(\boldsymbol{r},t)\right], \qquad (3)$$

where τ is the mean time of stay and n is the number of possible jump vectors, $\boldsymbol{s}_1 \ldots \boldsymbol{s}_n$. Per definition, G_{s} is a solution of (3) if the boundary condition $P(\boldsymbol{r},0) = \delta(\boldsymbol{r})$ is imposed. In the derivation of (3) the following assumptions have been applied: (I) Successive jumps are independent of each other; (II) the mean flight time from site to site is negligible compared to the mean time of stay; and (III) the jump probability is not influenced by the presence of protons at the neighbouring sites. Writing

$$G_{\text{s}}(\boldsymbol{r},t) = \int \exp\{-t\,f(\boldsymbol{\varkappa})\}\cdot\exp\{-i\,\boldsymbol{\varkappa}\,\boldsymbol{r}\}\,\mathrm{d}\,\boldsymbol{\varkappa} \qquad (4)$$

one finds

$$f(\boldsymbol{\varkappa}) = \sum_{\boldsymbol{s}_j}\left(1-\exp\{i\boldsymbol{\varkappa}\,\boldsymbol{s}_j\}\right)\cdot 1/n\,\tau\,. \qquad (5)$$

The Fourier transform of (4) gives a Lorentzian-shaped scattering law

$$S_{\text{inc}}(\boldsymbol{\varkappa},\omega) = \frac{1}{\pi}\,\frac{f(\boldsymbol{\varkappa})}{\omega^2+f^2(\boldsymbol{\varkappa})} \qquad (6)$$

with a half-width at half-maximum of $\Gamma = 2\,\hbar\,f(\boldsymbol{\varkappa})$.

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[3] B. ALEFELD, M. BIRR, and H. HEIDEMANN, Naturwiss. **56**, 410 [1969].

[4] C. CHUDLEY and R. ELLIOTT, Proc. Phys. Soc. London **77**, 353 [1961].

The function $f(\boldsymbol{\varkappa})$ is periodic in $\boldsymbol{\varkappa}$. For all $\boldsymbol{\varkappa}$-values approaching the reciprocal lattice vectors of the interstitial lattice the width becomes zero (this line narrowing is not to be confused with the line-narrowing for coherent scattering[5]). These $\boldsymbol{\varkappa}$-values are responsible for those Fourier components $\exp\{-t\,f(\boldsymbol{\varkappa})\}$ in (4) which no not decay for large t. It can be easily shown that they produce the asymptotic from of $G_s(\boldsymbol{r},t)$, namely the lattice sum of the interstitial arrangement with an envelope which is a Gaussian diffusion distribution

$$G_s(\boldsymbol{r},t) = (4\,\pi\,D\,t)^{-3/2}\exp\{-r^2/4\,D\,t\}\,.$$

In (3) it has been tacitly assumed that all interstitial positions are equivalent with regard to the set of jump vectors $\boldsymbol{s}_j$ which lead to the neighbouring sites. For more complicated interstitial arrangements this is not the case, i. e. the sites do not form a Bravais lattice. As can be inferred from Fig. 2, for octahedral or tetrahedral sites in a b.c.c. lattice there exist three or six types of positions, respectively. For instance, in the tetrahedral case, one obtains a system of six coupled rate equations of the type (3) and the scattering law consists of a sum of six Lorentzian like (6) with, in general, different half-widths[6].

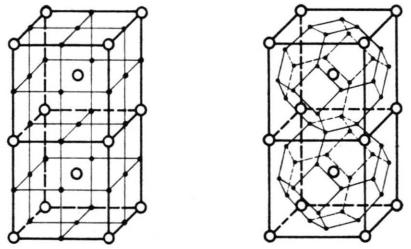

Fig. 2. Possible interstitial sites in a b.c.c. lattice: (a) octahedral, (b) tetrahedral positions. The jump distance is $a/2$ for (a), $a\sqrt{2}/4$ for (b) (a=edge length of the cubic cell).

A new approach has been worked out by Gissler and Rother[7] which seems to be easier to handle in cases of complicated interstitial lattices, including the possibility of multiple jumps. Assume that $W_N(\boldsymbol{r})$ is the probability that a diffusing atom arrives at $\boldsymbol{r}$ after having performed N diffusive jumps, when starting at $\boldsymbol{r}=0$. If $V_N(t)$ is the probability that N jumps have taken place during a time t, one has

$$G_s(\boldsymbol{r},t) = \sum_{N=0}^{\infty} W_N(\boldsymbol{r})\;V_N(t)\,. \tag{7}$$

From the theory of radio-active decay sequences one knows that

$$V_N(t) = \left(\frac{t}{\tau}\right)^N \frac{1}{N!}\exp\{-t/\tau\}\,. \tag{8}$$

One immediately sees that

$$W_0 = \delta(\boldsymbol{r})\,, \quad W_1 = \sum_{\boldsymbol{s}_j}\delta(\boldsymbol{r}-\boldsymbol{s}_j)\,.$$

The higher W's can be calculated by iteration according to the theory of the Markoff chains[8] until convergence is reached. Equation (7) can then readily be Fourier transformed to obtain $S_{\text{inc}}(\boldsymbol{\varkappa},\omega)$, Fig. 3 shows results for $\Gamma(\boldsymbol{\varkappa})$ for two different types of sites in a b.c.c. lattice as calculated by this method.

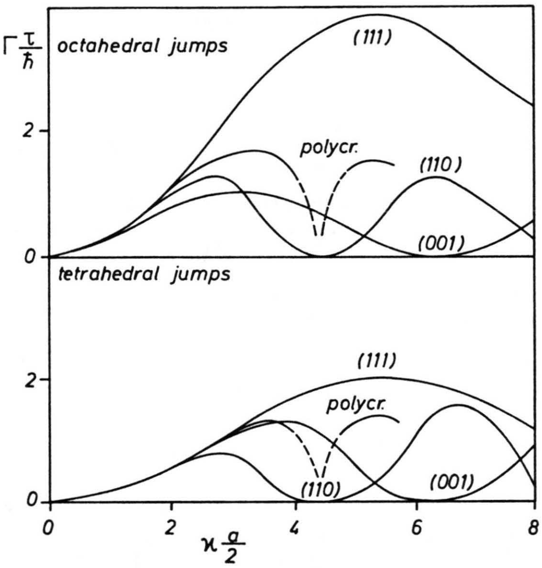

Fig. 3. Half-width of the quasi-elastic line times mean time of stay, τ, calculated as a function of the value of the scattering vector $\boldsymbol{\varkappa}$ for various direction of $\boldsymbol{\varkappa}$ for octahedral and tetrahedral jumps (see Fig. 2). From[7].

Experimental studies of quasi-elastic scattering on protons in metals have been performed by various authors. For the α-phase of palladium (Sköld and Nelin[9]) the occurrence of a maximum in the width $\Gamma(K)$ has been observed for the first time and it has been possible to decide conclusively in favour of an octahedral, rather than tetrahedral arrangement of the interstitial lattice. This decision became possible by the fact that the periodicities of both lattices differ strongly. This is not the case for the niobium-hydrogen system where both periods are equal (the tetrahedral and

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the octahedral case possess the same reciprocal lattice). By comparing the slope of $\Gamma(K)$ at small K and its value at some high value K^*, one finds a ratio $\Gamma(K^*)\,K^2\,a^2/\Gamma(K \to 0)$ which depends on the type of the interstitial lattice. This is shown across the critical temperature T_c in Fig. 4[10]. A strong change occurs at T_c which could be interpreted as a change in the type of the interstitial lattice. The interpretation must be discussed on the basis of the suggestion[11] that the phase transition in Nb – H can be described as a transition of a protonic "lattice gas" (α-phase) into a mixed phase ($\alpha + \alpha'$) where a "lattice gas" and "lattice liquid" are coexistent. As a consequence, the interpretation of the quasi-elastic scattering data in this two-phase region has to be taken with great caution. For the region $T > T_c$ one has also to consider the possibility of correlated multiple jumps[7]. Further studies on this system are underway.

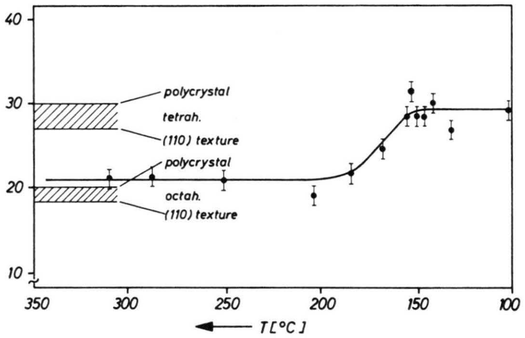

Fig. 4. Ratio of half-widths $\varkappa^2 a^2 \Gamma(\varkappa = \varkappa^* = 2.2\ \text{Å})/\Gamma(\varkappa \to 0)$ of quasi-elastic scattering from hydrogen in niobium as a function of temperature. The critical temperature is at 150 °C. The shaded areas indicate values expected theoretically for tetrahedral and octahedral jumps, respectively, taking into account texture of the polycrystalline samples. From [10].

A drastic reduction of the line width has been observed in the system vanadium – hydrogen[12] in passing from the α-phase (b.c.c.) to the (b.c.t.) β-phase. In this case the change can probably be ascribed to an ordering and a correspondingly strong change of the binding strength of the protons in the β-phase, due to the preferential filling of a certain fraction of the octahedral sites in the tetragonal lattice, for which there is more space available than for the other sites.

The neutron scattering experiments have further been applied to determine the self diffusion constant D, as $\Gamma(K)$ is proportional to $K^2 D$ for small K, the activation energy of D, and the jump rate[9, 10, 12, 13] $1/\tau$. Recent measurements of D and of the corresponding activation energies from an investigation of the mechanical relaxation caused by longrange diffusion[14] agree with the neutronic measurements within 10 percent which demonstrates the reliability of the method. For Nb – H and Pd – H the order of magnitude obtained from the experiments is 10^{-5} cm^2/s for D and 10^{12} s^{-1} for $1/\tau$. The values for V – H are even higher. This is the order of magnitude of D and $1/\tau$ as it is observed in liquid noble gases which demonstrates the extremely high mobility of the dissolved protons. On the other hand, the jump rate is still considerable smaller than the frequencies of the localized modes so that the assumption (I) leading to (3) remains still valid. The neglection of the flight time might become doubtful in the case of hydrogen in vanadium. It should be noticed that the jump rate is comparable with the frequencies of high energy phonons which might produce a damping mechanism.

An interesting subject is the intensity of the quasi-elastic peak. For defects performing harmonic vibrations it is proportional to the Debye-Waller factor which reads for an interstitial in cubic symmetry, $S_0(K) = e^{-\varkappa^2 \langle u^2 \rangle}$ where $\sqrt{\langle u^2 \rangle}$ is the average amplitude of the vibrating proton. The experiments[10] on Nb – H have demonstrated that the proton amplitude increases strongly as soon as the "lattice gas"-phase is reached. The corresponding value of $\langle u^2 \rangle$ increases from 0.10 to 0.18 Å^2. Similarly high values (up to 0.19 Å^2) have also been found for the system V – H at concentrations[12] below 20%. The proton amplitude estimated from the known oscillation frequencies for harmonic vibrations are much smaller. One finds for Nb – H with $h\,\omega_0 \cong 0.16$ eV for the localized mode[13] and for a host lattice contribution of $k_B\,\Theta \cong 0.02$ eV

$$\langle u^2 \rangle \cong \frac{\hbar^2}{2\,M_H\,\hbar\,\omega_0} + \frac{3\,\hbar^2\,k_B\,T}{M_{Nb}\,(k_B\,\Theta)^2} \cong 0.02\ \text{Å}^2.$$

This means that the wave function at the interstitial positions is anomalously extended in space at least for certain lattice directions. This statement should be seen in connection with the observation of the extremely high jump rates. For the future, an interesting problem would be the investigation of quasi-elastic neutron scattering on diffusing protons at low temperatures and concentrations where the diffusion can no longer be explained in a classical way as a thermally excited rate process[6, 15, 16]. Due to the smallness of D in this re-

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[14] G. SCHAUMANN, J. VÖLKL, and G. ALEFELD, Phys. Rev. Lett. **21**, 891 [1968].

[15] C. FLYNN and A. STONEHAM, Phys. Rev. B **1**, 3966 [1970].

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gion[14] the required energy resolution must be about ten times higher than has been employed so far.

3. Rotational Diffusion in Molecular Solids

In molecular solids the rotational motions of the molecules may be coupled, the angular displacements propagating through the system as waves (torsons) like optical phonons[17]; but the rotations also may be free or partly free. So far the high temperature phase of solid H_2 is the only known example for practically free rotations, but partly free rotations, that is rotational motions combining coupled librations and free rotations, appear in many molecular systems. The combination may be such that the motion is free in some angular coordinates and bound in others (example: the low temperature phase of solid H_2 and probably the high temperature phase of NH_4Cl) or such that the rotation of the molecule is bound for part of the time, and of a diffusive character for other parts of the time. This latter combination, which, of course, again can be different in the different coordinates, seems to be characteristic for instance for the plastic phases of organic crystals. In most of the high temperature phases of molecular crystals the orientational disorder probably is dynamical; the molecules or atomic groups at molecules fluctuate between different equilibrium orientations.

3.1. Rotation Jumps

The simplest combination of librations and free rotations is a motion alternating between librations and fast uncorrelated rotation jumps among different equilibrium orientations. In this case, if the mean time τ, for which a molecule oscillates around one equilibrium orientation, is large compared to the time, during which it rotates to the next orientation, we may write for the self correlation function

$$G_{\mathrm{s}}(\boldsymbol{r},t) = \frac{1}{n} \sum_{\nu=1}^{n} G_{\mathrm{L}}^{(\nu)}(\boldsymbol{r},t)\, G_{\mathrm{R}}^{(\nu)}(t) \tag{9}$$

with $G_{\mathrm{R}}^{(\nu)}(t)$ the probability that at time t the considered nucleus is at an equilibrium position ν, corresponding to a certain equilibrium orientation of the molecule, and $G_{\mathrm{L}}^{(\nu)}(\boldsymbol{r},t)$ the self correlation for the bound motions at site ν. n is the total number of such sites. If the jumps are uncorrelated, the $G_{\mathrm{R}}^{(\nu)}$ will obey rate equations[18, 19]

$$\frac{\mathrm{d}G_{\mathrm{R}}^{(\nu)}}{\mathrm{d}t} = \frac{1}{\tau}\left(-G_{\mathrm{R}}^{(\nu)} + \frac{1}{z}\sum_{\mu} G_{\mathrm{R}}^{(\mu)} \right), \tag{10}$$

where the sum goes over the z nearest equilibrium sites. The $G_{\mathrm{R}}^{(\nu)}$ are then exponential decay functions. By solving (2) under the conditions that

$$\sum_{\nu=1}^{n} G_{\mathrm{R}}^{(\nu)}(t) = 1; \quad G_{\mathrm{R}}^{(\nu)}(0) = \begin{cases} 1 & \text{for} \quad \nu = 1 \\ 0 & \text{for} \quad \nu \neq 1 \end{cases} \tag{11}$$

$$\text{and} \quad G_{\mathbf{R}}^{(\nu)}(t \to \infty) = \frac{1}{n}$$

one obtains

$$S_{\mathrm{inc}}(\boldsymbol{\varkappa},\omega) = \frac{1}{n}\sum_{\nu} \{ S_{\mathrm{el}}^{(\nu)}(\boldsymbol{\varkappa},\omega) + S_{\mathrm{R}}^{(\nu)}(\boldsymbol{\varkappa},\omega) + S_{\mathrm{L}}^{(\nu)}(\boldsymbol{\varkappa},\omega) + S_{\mathrm{RL}}^{(\nu)}\boldsymbol{\varkappa}\,(,\omega) \}$$

with S_{R} originating from the rotations jumps, S_{L} originating from the bound motions and S_{RL} a convolution of both. Experimentally the last two terms can be distinguished by their proportionality to $\varkappa^2$.

The first substance, in which such rotation jumps have been observed by quasi-elastic neutron scattering, is plastic solid adamantane[18] ($C_{10}H_{16}$). Figure 5 shows time-of-flight distributions of neutrons scattered a) in the brittle phase ($T < 208$ °K), b) in the plastic phase ($T > 208$ °K). The essential difference between the two distributions is the high intensity at small ω in the plastic phase. It could be quantitatively explained with rotation jumps. In the adamantane lattice, where $n = 6$, $z = 4$ (see insert Fig. 5), one obtains

$$\begin{aligned} S_{\mathrm{el}}^{(\nu)} + S_{\mathrm{R}}^{(\nu)} = e^{-2W} \Big\{ & \delta(\omega)\, \tfrac{1}{6}\, [1 + \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}_{\nu\mu'}) + \sum_{\mu \neq \mu'} \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}_{\nu\mu})] \\ & + \frac{1}{\pi}\, \frac{3/2\,\tau}{\omega^2 + (3/2\,\tau)^2}\, \tfrac{1}{3}\, [1 + \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}_{\nu\mu'}) - \tfrac{1}{2} \sum_{\mu \neq \mu'} \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}_{\nu\mu})] \\ & + \frac{1}{\pi}\, \frac{1/\tau}{\omega^2 + (1/\tau)^2}\, \tfrac{1}{2}\, [1 - \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}_{\nu\mu'})] \Big\}\,. \end{aligned} \tag{12}$$

In Fig. 6 values for τ obtained by neutron measurements are compared to values obtained by NMR[20]. Similar measurements have been done on $(NH_4)_2SO_4$ (l. c.[21]).

Equation (12) demonstrates, how neutron scattering may yield more information than NMR or other relaxation or optical measurements. We obtain a sharp elastic line, $\delta(\omega)$, corresponding to the bound de-

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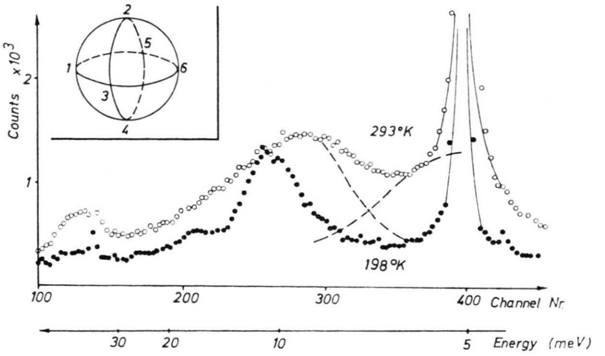

Fig. 5. Time-of-flight distribution of neutrons scattered from solid adamantane, a) at $T=198°$ (brittle phase), b) at $T=293$ K (plastic phase). The dashed line indicates qualitatively how the quasi-elastic scattering superimposes the elastic line and the spectrum of oscillatory lattice modes. From [18].

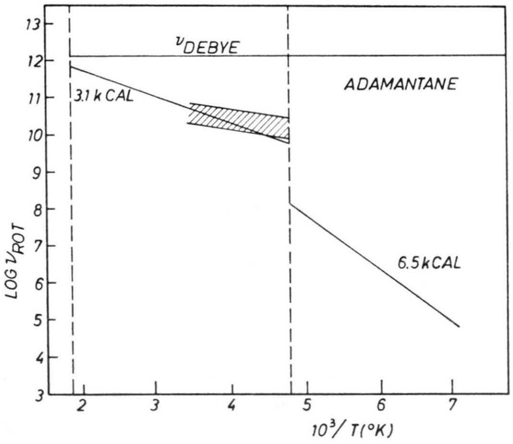

Fig. 6. Relaxation frequency of molecular re-orientation in adamantane, from NMR measurements [20] (solid lines) and from neutron scattering [18] (shaded area). The latter values were obtained by a computer fit to the experimental data.

grees of freedom, superimposed on Lorentzians originating from the rotation jumps. The Debye-Waller factor $\exp\{-2\,W(\boldsymbol{\varkappa})\}$ is determined by the amplitudes of the bound motions. In addition, however, each term in (12) is associated with a further function of $\boldsymbol{\varkappa}$; the cos-terms represent diffraction patterns resulting from interferences of waves, which are scattered from a proton seen simultaneously at different equilibrium sites; the $\boldsymbol{l}_{\nu\mu}$ are the distances of these sites, the index μ' specifying the position not neighbouring to ν. Upon integration over ω these diffraction patterns disappear. By their observation the equilibrium orientations can be determined. More complicated diffraction patterns will appear, if the rotations are due to quantum-mechanical tunneling, because then the regions of overlap between the equilibrium sites also give rise to interferences (Section 4). In this way classical and quantum-mechanical transitions may be distinguished.

If a transition to an ordered phase is approached, some orientations may become prefered, so that Eq. (10) must be generalized to

$$\frac{\mathrm{d}G_{\mathrm{R}}^{(\nu)}}{\mathrm{d}t} = -\frac{1}{\tau^{(\nu)}}\,G_{\mathrm{R}}^{(\nu)} + \frac{1}{\mathrm{z}}\sum_{\mu}\frac{1}{\tau^{(\mu)}}\,G_{\mathrm{R}}^{(\mu)}\,,$$

and the last one of the conditions (11) is to be replaced by

$$G_{\mathrm{R}}^{(\nu)}\,(t\to\infty) = \frac{\tau^{(\nu)}}{\tau^{(\mu)}}\,G_{\mathrm{R}}^{(\mu)}\,(t\to\infty)\,.$$

The width of the Lorentzians then will be determined by a mean relaxation time

$$\frac{1}{\tau} = \sum_{\nu}\frac{G_{\mathrm{R}}^{(\nu)}\,(t\to\infty)}{\tau^{(\nu)}}\,.$$

In going over the phase transition some of the τ may increase and others decrease. No singularity is to be expected, however, just as there is no singularity in the self-diffusion constants for the components of alloys [22]. Only the derivative of τ with respect to temperature may exhibit a singularity.

3.2. *Continuous Rotational Diffusion*

In general the jump time may not be small compared to the time the molecule is bound in librations. The molecules may perform slow continuous diffusive motions between the equilibrium orientations, and finally the equilibrium orientations themselves may become ill-defined. The self-correlation then can no longer be described by a finite number of rate equations.

A case opposite to the one considered in the preceding section, namely an isotropic system, a molecular liquid, has been treated by LARSSON and BERGSTEDT [23], by LARSSON [24], by SEARS [25], and by EGELSTAFF [26] for linear and for spherical molecules. In the following we outline a combination of these theories *. The rotational motions are assumed to alternate between jumps and a continuous rotational diffusion combined with librations, the center of gravity motions are assumed to alternate between vibrations and diffusion. Like for the description of hydrogen motions in metals (Section 2) the self-correlation $G_{\mathrm{s}}(\boldsymbol{r},t)$ is represented as a sum over all possible ways, in which a nucleus

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* Upon completion of this paper we learned that such a combination has been worked out by Larsson and will be published in Physical Review. Unfortunately this work has not been available to us.

may travel in time t from the origin to $\boldsymbol{r}$. The different ways are different sequences $H_m(\boldsymbol{r}, t)$ of steps of alternations between the different kinds of motions. All motions are supposed uncoupled, so that each step is a convolution of probabilities for the different motions. For instance, if at $t=0$ the center of gravity is in a vibratory state, the first step is

$$H_0(\boldsymbol{r}\,, t) = \int \mathrm{d}\boldsymbol{r}'\, g_\mathrm{e}(\boldsymbol{r}', t)\, p_\mathrm{e}(t) \sum_{n=0}^{\infty} F_n(\boldsymbol{r} - \boldsymbol{r}', t),$$

if $g_\mathrm{e}(\boldsymbol{r}', t)$ is the probability, that the center of gravity is vibrating at time t at $\boldsymbol{r}'$, if at time 0 it was at $\boldsymbol{r}'=0$, $p_\mathrm{e}(t)$ the probability, that at time t it still is in a vibratory state, and $F_n(\boldsymbol{r}-\boldsymbol{r}', t)$ the probability that during this time the considered nucleus has moved in n steps, alternating between the two kinds of rotational motions of the molecule, from $\boldsymbol{r}-\boldsymbol{r}'=0$ to $\boldsymbol{r}-\boldsymbol{r}'$. The next step is then

$$\begin{aligned} H_1(\boldsymbol{r}\,, t) = \int_0^t \mathrm{d}t_1 \int \mathrm{d}\boldsymbol{r}_1\, q_\mathrm{e}(t-t_1) \int \mathrm{d}\boldsymbol{r}'\, h_\mathrm{e}(\boldsymbol{r}'-\boldsymbol{r}_1\,, t-t_1) \\ \cdot \sum_n F_n(\boldsymbol{r}-\boldsymbol{r}_1-\boldsymbol{r}'+\boldsymbol{r}_1', t-t_1) \\ \times \int \mathrm{d}\boldsymbol{r}_1'\, g_\mathrm{e}(\boldsymbol{r}_1', t)\,[1-p_\mathrm{e}(t_1)] \sum_n F_n(\boldsymbol{r}_1-\boldsymbol{r}_1', t_1) \end{aligned}$$

with $1-p_\mathrm{e}(t)$ the probability, that during t the center of gravity goes from a vibratory to a diffusive motion, $q_\mathrm{e}(t)$ the probability that it remains in diffusive motion, $h_\mathrm{e}(\boldsymbol{r}, t)$ the probability, that it is vibrating at time t at $\boldsymbol{r}$, if at time 0 it was at $\boldsymbol{r}=0$, etc.

For the F_n, for the rotational motions, corresponding probabilities are defined, namely a probability $h_\mathrm{i}(\boldsymbol{r}, t)$ that a nucleus, which at time 0 was at the origin, arrives at time t at $\boldsymbol{r}$ by a rotational jump with the molecule, with a probability $p_\mathrm{i}(t)$ analogous to $p_\mathrm{e}(t)$, and a probability $g_\mathrm{i}(\boldsymbol{r}, t)$, that the nucleus, which was at the origin at $t=0$, is at time t librating and simultaneously following small diffusive molecular rotations at $\boldsymbol{r}$,

$$g_i(\boldsymbol{r}\,, t) = \int \mathrm{d}\boldsymbol{r}'\, g_{i\mathrm{R}}(\boldsymbol{r}', t)\, g_{i\mathrm{L}}(\boldsymbol{r}-\boldsymbol{r}', t), \qquad (13)$$

with a probability $p_\mathrm{i}(t)$, that it was in the same motion at $t=0$. Then

$$G_\mathrm{s}(\boldsymbol{r}, t) = \sum_{m=0}^{\infty} [H_{2m}(\boldsymbol{r}, t) + H_{2m+1}(\boldsymbol{r}, t)] \qquad (14)$$

with the second term for the case, that at the beginning the center of gravity is diffusing.

A detailed model for the dynamics of the system is formulated by assumptions with respect to the various probabilities. For this formulation one encounters the difficulty that for the rotational motions it must be given in angular coordinates. In the original version of the theory of LARSSON[24] this difficulty was avoided by approximating the motions on spheres around the centers of gravity by motions on planes tangential to the spheres, but this approximation has the serious consequence that the self-correlation functions all become zero for $t \to \infty$. As first shown by SEARS[25] for an isotropic system of linear or spherical molecules the difficulty can be overcome by a $\varkappa$-expansion of the Fourier transforms of the correlation functions with respect to $\boldsymbol{r}$ as a series of spherical harmonics, for instance

$$\begin{aligned} \hat{h}_\mathrm{i}(\boldsymbol{\varkappa}\,, t) &= \frac{1}{(2\,\pi)^3} \int h_\mathrm{i}(\boldsymbol{r}\,, t) \exp\{i \boldsymbol{\varkappa}\, \boldsymbol{r}\}\, \mathrm{d}\boldsymbol{r} \\ &= \langle \exp\{i \boldsymbol{\varkappa}\, (\boldsymbol{d}\,(t) - \boldsymbol{d}\,(0))\}\rangle_{h_\mathrm{i}} \qquad (15) \\ &= \sum_{l=0}^{\infty} (2\,l+1)\; j_l^2(\varkappa\, d)\; \tilde{h}_\mathrm{i}^l(t), \end{aligned}$$

if $\boldsymbol{d} = \boldsymbol{R} - \boldsymbol{r}$ is the position of the nucleus relative to the position $\boldsymbol{R}$ of the center of gravity. The $j_l(x)$ are spherical Bessel functions of order l,

$$\tilde{h}_\mathrm{i}^l(t) = (2\,l+1)\, \langle P_l(\cos\Theta(t))\, P_l(\cos\Theta(0))\rangle_{h_\mathrm{i}} \qquad (16)$$

is an orientation corelation function with P_l a Legendre polynomial, Θ the orientation of the molecule to an axis fixed in space.

The following assumptions may be made:

i) for the center of gravity diffusion

$$\hat{h}_\mathrm{e}(\boldsymbol{\varkappa}\,, t) = \exp\{-\varkappa^2 D_\mathrm{e}\, t\}; \quad q_\mathrm{e}(t) = \exp\{-t/\tau_{\mathrm{e}1}\};$$

ii) for the center of gravity vibrations

$$\begin{aligned} \hat{g}_\mathrm{e}(\boldsymbol{\varkappa}, t) &= \exp\{-\tfrac{1}{3}\,\varkappa^2\langle u^2\rangle\}\,(1+\langle \boldsymbol{\varkappa}\, \boldsymbol{u}\,(t)\; \boldsymbol{\varkappa}\, \boldsymbol{u}\;(0)\rangle); \\ p_\mathrm{e}(t) &= \exp\{-t/\tau_{\mathrm{e}0}\}, \end{aligned}$$

that is: a phonon expansion[1], the center of gravity displacements $\boldsymbol{u}\;(t)$ are taken to be undamped plane waves[27];

iii) for the rotation jumps[26, 28]

$$\begin{aligned} \hat{h}_\mathrm{i}(\boldsymbol{\varkappa}, t) &= \sum_l\, (2\,l+1)\; j_l^2(\varkappa\, d)\, \exp\{-(\varDelta\omega)_l\, t\}; \\ q_\mathrm{i}(t) &= \exp\{-t/\tau_{\mathrm{i}1}\} \end{aligned}$$

with

$$(\varDelta\omega)_l = \frac{1}{\tau_{\mathrm{i}1}} \left(1 - \frac{1}{2\,l+1} \int_0^\pi \mathrm{d}\varepsilon\; W(\varepsilon)\, \frac{\sin(l+\frac{1}{2})\,\varepsilon}{\sin\frac{1}{2}\,\varepsilon}\right),$$

$$W(\varepsilon) = \tfrac{1}{2}\left[1 + \left[\frac{2}{\vartheta}\right)^2\right] \sin(\tfrac{1}{2}\,\varepsilon)\, \exp\{-\varepsilon/\vartheta\}\,.$$

iv) for the librational diffusive state (13)

$$\hat{g}_{\mathrm{iL}}(\boldsymbol{\varkappa}\,, t) = \exp\{-\tfrac{1}{2}\,\varkappa^2\langle w^2\rangle\}\,(1+\langle\, \boldsymbol{\varkappa}\, \boldsymbol{w}\;(t)\; \boldsymbol{\varkappa}\, \boldsymbol{w}\;(0)\rangle)$$

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in analogy to $\hat{g}_e(\boldsymbol{\varkappa}, t)$, and [25]

$$g_{iR}(\boldsymbol{\varkappa}, t) = \sum_l (2\,l+1)\; j_l^2(\varkappa\, d)\, \exp\{-l(l+1)\, D_R\, t\}\,;$$

$$p_i(t) = \exp\{-t/\tau_{i0}\}\,.$$

The complex motion is thus desribed by 9 parameters: the self-diffusion constant D_e for the center of gravity diffusion, the mean life time τ_{e1} of this diffusive state, the mean square amplitude $\langle u^2 \rangle$ of the center of gravity vibrations, the mean life time τ_{e0} of such a vibrational state, the mean angular displacement ϑ in rotational jump motions, their mean duration τ_{i1}, the square amplitude $\langle w^2 \rangle$ of the librations, a diffusion constant D_R for small rotational displacements and the mean life time τ_{i0} of this librational-diffusive state. The translatory amplitudes $\langle u^2 \rangle$ are assumed isotropic, the cloud of librational ampltiudes $\langle w^2 \rangle$ is assumed circular [29]. The diffusive motions are supposed to obey simple diffusion laws. A better description may be Langevin diffusion as formulated for translatory motions by EGELSTAFF and SCHOFIELD [30] and for rotational motions by EGELSTAFF [26]; this would introduce, however, two further parameters.

The resulting quasi-elastic scattering is again a composition of Lorentzians and, eventually, δ-functions, corresponding to the different kinds of motions. Unfortunately, with systems, to which the theories may apply, so far measurements could not be performed with sufficient accuracy to provide a test for the validity of the various assumptions in the above description of the molecular motions. A very interesting comparison of neutron measurements [31] with Rayleigh and Raman scattering [32] on plastic cyclohexane suggests the presence of strong cooperative phenomena in the rotational behaviour of the molecules [26].

The measurements require very high resolution. Moreover, with such systems it will be particularly difficult to separate the quasi-elastic from inelastic scattering, which arises from the terms $\langle \boldsymbol{\varkappa}\, \boldsymbol{u}(t)\, \boldsymbol{\varkappa}\, \boldsymbol{u}(0) \rangle$ and $\langle \boldsymbol{\varkappa} \boldsymbol{w}(t)\, \boldsymbol{\varkappa} \boldsymbol{w}\,(0) \rangle$ and to which, in addition, eventual free rotations may contribute. To our knowledge so far for a system with molecules without fixed equilibrium orientations a decomposition of the quasi-elastic scattering into components of different widths has been observed clearly only once, by high resolution measurements on solid CH_4 at 16 °K [33]. The absence of equilibrium orientations for some of the molecules here seems to be established by recent neutron diffraction measurements on solid CD_4 [34]; unfortunately the observations [33] are not yet evaluated. A similar decomposition is suggested for liquid glycerol by high resolution measurements performed at the FMR reactor in Munich with the back scattering spectrometer mentioned in the introduction [35]. In contrast to earlier observations [36, 37] the broadening of the elastic scattering was found to be very small, the width corresponding to the translatory self-diffusion, D_e, alone. But the intensity of this scattering was only a fraction of the total scattering, so that there may be a broad distribution underneath the observed one, the broad distribution being unobserved owing to too high resolution. Figure 7 shows values for the translatory self-diffusion constant in liquid glycerol as obtained by different experimental techniques.

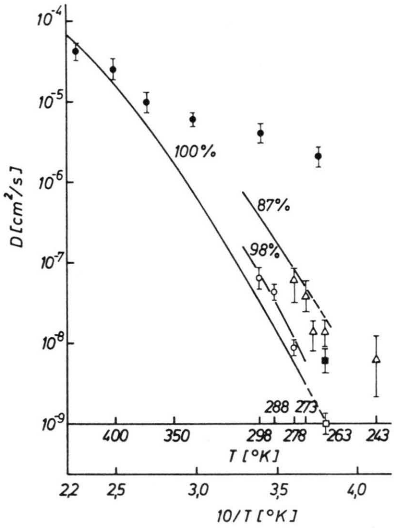

Fig. 7. Comparison of different measurements of the translatory diffusion constant D_e in glycerol. Solid lines = from viscosity measurements, □ CoCl tracer in 99.5% glycerol, ■ CoCl tracer in 93% glycerol, ● neutron measurements by LARSSON et al., 99.5% glycerol; neutron measurements by BIRR with the new type of spectrometer at the FRM reactor in Munich, △ 87%, ○ 98% glcerol (from [35]).

3.3. Angular Momentum Diffusion

In the preceding sections we considered molecules freely rotating for part of the time and librating for other parts of the time. As already mentioned, free and bound rotational motions also may be combined such that they are free in some and bound in other angular coordinates. This can be described as an

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intermolecular coupling of angular momenta with respect to the free components. In solid f.c.c. H_2 for instance these momenta are ordered, their coupled precessions giving rise to angular momentum waves[38] analogous to spin waves. If the analogy is carried further, it seems possible that at temperatures above a phase of ordered angular momenta there also may be a diffusion of the angular momentum density analogous to spin diffusion in paramagnets[39]. Such motions may be observable as (coherent) quasi-elastic critical scattering around Bragg reflections, and here one might expect singularities at phase transitions. However, so far this problem has not yet been studied, neither experimentally nor theoretically.

4. Proton Tunneling at Hydrogen Bonds

The diffraction pattern resulting from interferences of waves scattered from a nucleus, which is seen simultaneously at several equilibrium positions, can be used not only for identifying rotation jumps of molecules (Section 3.1) but, of course, also for observing fluctuations of individual nuclei, for instance the fluctuations of protons between two equilibrium sites in hydrogen bonds[40]. The condition for the appearance of such diffraction patterns is, that the time, for which a neutron wave packet travels over the atom, be larger than the mean time τ the nucleus stays at one equilibrium site, that is: the resolution in ω must be $\Delta\omega < 2\pi/\tau$. Hence for motions with large τ high resolution may be required. The second condition is, that $\varkappa$ must be comparable to l^{-1}, if l is the distance of the equilibrium sites. Thus small $\Delta\omega$ and large $\varkappa$ may be necessary at the same time.

Whether such fluctuations of protons in H-bonds give rise to quasi-elastic or to inelastic scattering depends on the kind of correlations affecting them. In the simplest case, uncorrelated fluctuations between two fixed sites with a tunneling mechanism, the proton ground states are

$$\psi_1 = C_{1l}\,\Phi_l + C_{1r}\,\Phi_r\,, \psi_2 = C_{2l}\,\Phi_l + C_{2r}\,\Phi_r\,, \quad (17)$$

if Φ_l and Φ_r are the ground states on the left and the right site, respectively, for a wide separation of the two sites. From these states one obtains with harmonic oscillator functions for the Φ[41]

$$\begin{aligned} S_{\text{inc}}(\boldsymbol{\varkappa}, \omega) = e^{-2W} \{ & \delta(\omega)\,[C_1 + C_2 \cos(\boldsymbol{k}\,\boldsymbol{l}) + C_3 \cos(\tfrac{1}{2}\,\boldsymbol{\varkappa}\,\boldsymbol{l})] \\ & + [p_1\,\delta(\omega+\omega_t) + p_2\,\delta(\omega-\omega_t)]\,[C_1' + C_2' \cos(\boldsymbol{\varkappa}\,\boldsymbol{l}) + C_3' \cos(\tfrac{1}{2}\,\boldsymbol{\varkappa}\,\boldsymbol{l})]\} \end{aligned} \quad (18)$$

that is: a sharp elastic and two equally sharp inelastic lines representing a transition between ψ_1 and ψ_2. $\omega_t = \hbar^{-1} \cdot (E_2 - E_1)$ is the tunneling frequency, with E_2 the energy of ψ_2, E_1 the energy of ψ_1. The cos-terms represent diffraction patterns analogous to those of Eq. (12), l is the distance of the two equilibrium positions.

The term $\cos(\frac{1}{2}\boldsymbol{\varkappa}\boldsymbol{l})$ represents an interference of waves scattered from either one of the two density maxima in distance $\boldsymbol{l}$ and the region of overlap in the center between them, that is: it is a direct consequence of the quantum mechanism. The coefficients C and C' are combinations of the expansion coefficients in (17), together with the thermal occupations $P_{1/2}$ of ψ_1 and ψ_2 and the value of the overlap integral[41]. With a determination of these coefficients one obtains the parameter values for the hydrogen bond potential. The Debye-Waller factor originates from the proton amplitudes at the equilibrium positions. If the protons are correlated in their fluctuations, as one must assume in crystalline systems of H-bonds, then a spectrum of tunnel frequencies is to be expected[42, 43]. This spectrum may extend to or even become centered[42] at $\omega = 0$.

For many systems of hydrogen bonds the question whether the protons have one or two equilibrium sites is an unsolved problem[40, 44]. Even less answered is the problem of whether and how they fluctuate, if there are two sites. Both problems have been widely discussed in particular for the ferroelectrics of the type KH_2PO_4, because many properties of these substances can be understood, if for the paraelectric phase such fluctuations are assumed, coupled such that always two protons only are on positions close to a PO_4 group and, in addition, coupled to certain lattice modes[45]. Recently experiments with elastic incoherent neutron scattering[46] have revealed a diffraction pattern as shown in Fig. 8. The observed pattern is compared to a pattern

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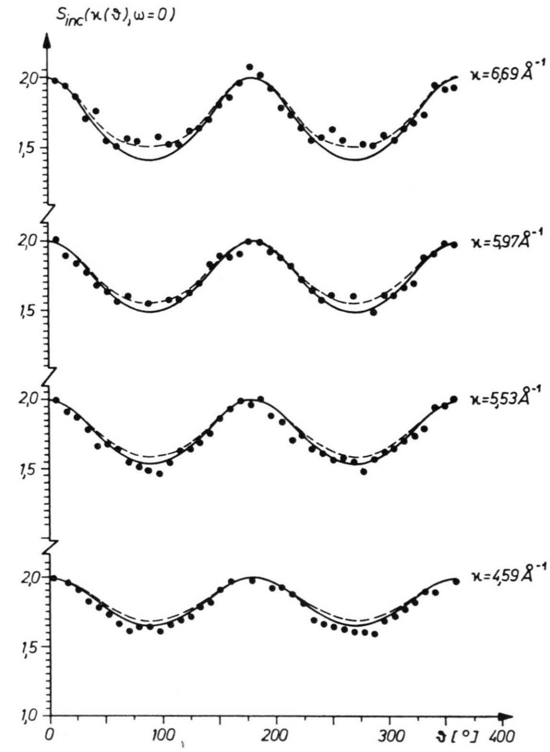

Fig. 8. Diffraction pattern in elastic incoherent neutron scattering from a paralectric single crystal of KH_2PO_4 ($\frac{1}{2}\pi - \vartheta$) is the angle between K and one of the directions of hydrogen bond. – – – – = best fit with the tunneling proton model; ——— = best fit with an anisotropic single oscillator model (from [46]).

as to be expected from the elastic part of the scattering law (18) as well as to patterns as to be expected for protons located in the center between neighbouring oxygen atoms but with an amplitude elongated in the direction of the 0 – 0 line. The comparison supports the assumption of tunnel fluctuations. If these observations are taken together with the results of recent infrared measurements [47], which have shown that the proton amplitudes actually are smaller in the 0 – 0 direction than in the directions perpendicular to it, then the fluctuations between two sites can be considered as experimentally proven. Figure 9 shows how, in approaching the ferroelectric transition, the diffraction pattern disappears; the proton density distribution is contracted; the protons become trapped on ordered sites.

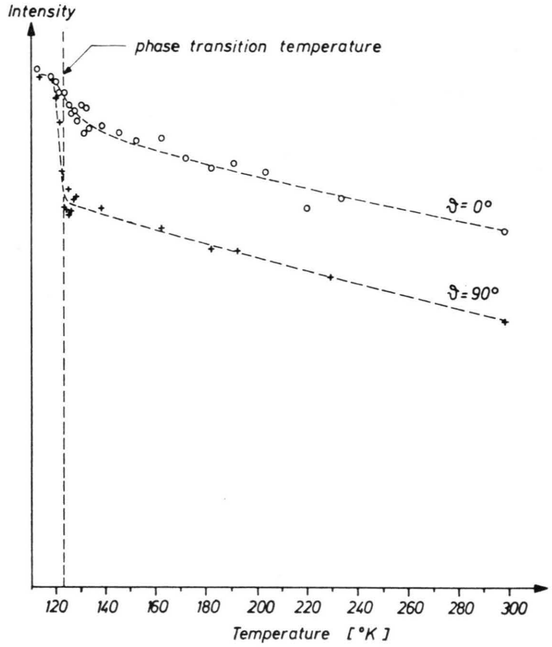

Fig. 9. Intensity of elastic neutron scattering for $\vartheta = 0$ (maximum in the diffraction pattern of Fig. 8) and for $\vartheta = \frac{1}{2}\pi$ (minimum in the diffraction pattern) as a function of temperature (from [46]).

A detailed analysis of the neutron observations has also shown that the scattering law (18) describes only the essential features of these fluctuations. For a consistent fit the influence of the motions of the neighbouring atoms had to be taken into account [46]. Sharp peaks in inelastic scattering, as predicted by Eq. (18), also where not observed.

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