

COLLECTIVE MOTIONS OF HYDROGEN BONDS

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The low frequency collective modes of protons are calculated for ferroelectric crystals of the KH_2PO_4 type taking into account the tunneling frequency and a simplified interaction between proton sites. They give rise to a band of frequencies which could be observed by inelastic scattering of neutrons. (In the deuterated salts, on the other hand the band is very narrow and the excitations are only weakly coupled to the neutrons). When the temperature is raised, there is a decrease in frequency and a broadening for each mode. Finally, in the paraelectric state, one expects a broad neutron spectrum from the hydrogen compound, but only quasielastic scattering from the deuterium compound.

In the ferroelectric phase of KH_2PO_4 the protons take a known ordered configuration¹. What are the elementary excitations from this ordered state? Since each proton moves in a strongly anharmonic potential well, these excitations cannot be described simply as phonons. We discuss them in the following approximation: each proton (i) can occupy one of two states ψ_{2i} , ψ_{1i} (corresponding to the two minima of the potential well). We ascribe a fictitious spin $S_i = 1/2$ to the (i)th proton, such that $S_{zi} = +1/2$ corresponds to state ψ_{2i} , and $S_{zi} = -1/2$ to ψ_{1i} . The energy of the proton system will be of the form

$$\chi = 2 \Omega_T \sum_i S_{xi} - \sum_{ij} J_{ij} S_{zi} S_{zj} \quad (1)$$

where Ω_T is the tunneling integral², and J_{ij} describes an interaction between proton sites, comprising direct electrostatic effects and indirect couplings through the PO_4 groups. Eq(1) represents an extreme simplification: 1) higher vibrational states of the proton are not included (this is not too serious since they are probably in the 2000 cm^{-1} range, while the frequencies to be considered are of order $\Omega_T \sim 200 \text{ cm}^{-1}$. 2) Interactions between the proton and the vibrational modes of neighbouring atoms although important³ are not explicitly written down. In the weak coupling limit they would again lead to an interaction between protons of the $J_{ij} S_{zi} S_{zj}$ type, but retarded in time. 3) Possible effects of one proton on the tunneling integral of another proton (corresponding to interactions of the form $B_{ij} S_{xi} S_{zj}$) are not taken into account.

The physical model corresponding to eq. (1) has been introduced by Blinc⁴.

The ground state of χ is easily derived in the semi classical approximation putting $S_{zi} = 1/2 \cos \theta$, $S_{xi} = 1/2 \sin \theta$, the energy per proton is⁵

$$E = \Omega_T \sin \theta - \frac{1}{4} \cos^2 \theta J \quad (2)$$

$$J = \sum_j J_{ij} > 0$$

(where

and it is a minimum for

$$\sin \theta = - \frac{2 \Omega_T}{J} \quad (3)$$

Eq.(3) describes a partially polarised ground state, and is valid when $\Omega_T < J/2$. (When $\Omega_T > J/2$ the ground state is not polarised). To derive the elementary excitations it is convenient to rotate the reference frame by an angle θ , putting

$$\begin{aligned} S_{zi} &= S_{zi}' \cos \theta - S_{xi}' \sin \theta \\ S_{xi} &= S_{zi}' \sin \theta + S_{xi}' \cos \theta \end{aligned} \quad (4)$$

Then write down the equations of motion $\frac{d S_{x'}}{dt} = i [\chi, S_{x'}]$, and linearise them (replacing S_z by 1/2 and retaining only first order terms in $S_{x'}$, $S_{y'}$). Look for solutions of the form $S_{xi} = S_x e^{i(\omega t - k \cdot R_i)}$, etc .. The result is :

$$\left. \begin{aligned} i \omega S_{x'} &= J S_{y'} \\ i \omega S_{y'} &= - [J - J(k) \sin^2 \theta] S_{x'} \end{aligned} \right\} \quad (5)$$

$$J(k) = \sum_j J_{ij} e^{i k(R_j - R_i)} \quad (6)$$

The dispersion relation derived from eq.(5) is :

$$\omega(k) = [J (J - J(k) \sin^2 \theta)]^{1/2} \quad (7)$$

For short range interactions $J(k)$ is well defined in the limit $k \rightarrow 0$ ⁶. Then the lowest excitation frequency ω_{\min} corresponds to $k = 0$ ⁷

$$\omega_{\min} = \sqrt{J^2 - 4 \Omega_T^2} \quad (8)$$

To get the highest excitation frequency ω_{\max} we must specify $J(k)$ = for instance, with a simple cubic lattice of protons and nearest neighbour interactions the minimum of $J(k)$ is

- J and $\omega_{\max} = \sqrt{J^2 + 4 \Omega_T^2}$. For KH_2PO_4 we estimate $J = 420^\circ\text{K}$ and $\sin \Theta = 0.9$ from the molecular field calculation of Blinc⁴. Then we expect $\omega_{\min} \sim 200^\circ\text{K}$ and $\omega_{\max} \sim 600^\circ\text{K}$. For KD_2PO_4 on the other hand we expect $\Omega_T < J$ (tunneling by a deuteron being slow) and the band width ($\sim \Omega_T^2$) is very small.

We now consider the general features of the neutron scattering by one hydrogen bond, in terms of the fictitious spins S_i . If a is the scattering length of the proton, we may define a scattering operator

$$a_i(\underline{k}) = a \left[\alpha(\underline{k}) + 2\beta(\underline{k}) S_{zi} + 2\gamma(\underline{k}) S_{xi} + 2\delta(\underline{k}) S_{yi} \right] \quad (9)$$

The matrix element of a_i between two states of the proton (i) give us the scattering amplitude for the process where the proton goes from state 1 to state 2, the neutron wave vector being increased by the amount \underline{k} . Again all transitions to higher vibrational states of the proton are neglected. The form factors α, β, γ are given by

$$\begin{aligned} \alpha(\underline{k}) &= \int \frac{\varphi_l(\underline{r})^2 + \varphi_r(\underline{r})^2}{2} e^{i \underline{k} \cdot \underline{r}} d_3r \\ \beta(\underline{k}) &= \int \frac{\varphi_l(\underline{r})^2 - \varphi_r(\underline{r})^2}{2} e^{i \underline{k} \cdot \underline{r}} d_3r \\ \gamma(\underline{k}) &= \int \varphi_l(\underline{r}) \varphi_r(\underline{r}) e^{i \underline{k} \cdot \underline{r}} d_3r \end{aligned} \quad (10)$$

The basis functions φ_l, φ_r are again assumed real, in which case $\delta = 0$. In full rigor the form factors should depend on the vibration amplitudes of the neighboring atoms. In the following, we treat them as constants, (thereby neglecting some mixed scattering events where both phonons and collective proton modes would be excited). In practice it is convenient to choose the origin of coordinates in (10) at the mid point \underline{R} of the hydrogen bond. If \underline{R} is a center of symmetry, α and γ are then real and β is pure imaginary. If there is a plane of symmetry (normal to the bond direction) passing by point \underline{R} , β is 0 when \underline{k} is in this plane. Finally, we note that γ depends on an overlap integral; γ will probably be very small for a D atom, and still rather small for H.

Using eq.(9), the incoherent scattering cross section per proton (for momentum transfer \underline{k} and energy transfer ω to the neutron) can be written in the Van Hove form⁸

$$\frac{d\sigma}{d\Omega d\omega} = \frac{k_f}{k_0} a_{\text{inc}}^2 \int \frac{dt}{2\pi} e^{i\omega t} (\alpha(\underline{k}) + 2\beta(\underline{k}) S_{zi}(0) + 2\gamma(\underline{k}) S_{xi}(0)) (\alpha(\underline{k}) + 2\beta(\underline{k}) S_{zi}(t) + 2\gamma(\underline{k}) S_{xi}(t)) \quad (11)$$

where $S_i(t) = e^{iHt} S_i e^{-iHt}$ is the Heisenberg operator describing the spontaneous motion

of the spin S . k_0 and k_1 are the initial and final neutron momenta. A similar formula (involving correlations between two different "spins" $S_i S_j$) is obtained for coherent scattering.

The physical conclusion is that the neutrons give us informations on the motions of S_{zi} (except for some very special scattering situations where $\beta = 0$ and γ survives alone).

a) In a hydrogen compound like KH_2PO_4 the modes (7) correspond to a finite modulation of S_z , and are thus observable by neutron scattering. The scattering being mainly incoherent in this case, they will give rise to a broad spectrum of energies extending from ω_{\min} to ω_{\max} . To work with well defined modes the temperatures should be significantly lower than T_c and to have a reasonable intensity the processes in which the neutrons give energy to the excitations should be investigated. b) In KD_2PO_4 , since Ω_T is small each S_{zi} is nearly a constant of the motion and the collective modes cannot be excited by neutrons. We shall finally give a brief discussion of temperature effects: when T increases the frequencies (7) decrease and also each mode increases in linewidth. At low temperatures these effects could be computed by standard procedures. It is of interest to go to the opposite limit of temperatures much higher than the transition point. The correlation function which is measured in practice is $\langle S_{zi}(0) S_{zi}(t) \rangle$ (for incoherent scattering or even for coherent scattering by polycrystals provided that k is large⁹). The results will be very different depending on the ratio Ω_T/J .

a) For $\Omega_T \ll J$ (deuterium compounds) we can think of the tunneling term as a perturbation inducing transitions between $S_z = \pm 1/2$ levels. To ensure energy conservation, this transition will be allowed only when the field (due to the J interaction) vanishes. Assuming a gaussian distribution for this field we get a rate of flip

$$W_{+-} = (2\pi)^{1/2} \frac{\Omega_T^2}{J_2} \quad (12)$$

$$(J_2^2 = \sum_j J_{ij}^2)$$

The neutron spectrum in this case will be a lorentzian of half width $2W_{+-}$ (very small): the scattering is quasi elastic. Note that in some cases the transitions W_{+-} might be slow enough to give a significant contribution to the nuclear relaxation of deuterium by modulation of the electric field gradient.

b) For $\Omega_T \gg J$ the hamiltonian (1) is formally similar to a system of nuclear dipoles in a rigid lattice submitted to an external field $2\Omega_T$ and coupled by non-scalar interactions. We expect to find a neutron line at the frequency $2\Omega_T$ with a more or less gaussian shape. The second moment can be computed after suitable truncation of χ^{10} and is given by $\Delta\omega^2 = 1/16 J_2^2$. Thus the line width is of order J_2 . It may be of interest to measure the interaction J_{ij} by this method in crystals where the hydrogen bonds do not display a cooperative transition because Ω_T is too large.

c) For $\Omega_T \sim J$ (case of KH_2PO_4) we expect a more or less gaussian spectrum centered on $\omega = 0$. The second and fourth moments of the spectrum can be calculated in the limit of complete disorder¹¹ :

$$\begin{aligned}\langle \omega^2 \rangle &= 4 \Omega_T^2 \\ \langle \omega^4 \rangle &= 4 \Omega_T^2 (4 \Omega_T^2 + J_2^2)\end{aligned}\tag{13}$$

In conclusion we except collective modes of hydrogen bonds in materials like KH_2PO_4 ; the main difference between low temperature and high temperature scattering (apart from intensity factors) is that for $T < T_c$ we expect a spectrum extending from ω_{\min} to ω_{\max} , while for $T \gg T_c$ we expect a spectrum centered around 0 frequency. We emphasise again that the model considered here is extremely primitive since it neglects many effects related to the interactions between hydrogen bonds and lattice vibrations : these interactions will in fact be particularly important near crossovers between phonon branches and collective mode branches.

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References

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2. We take the φ 's as real functions : then there are no terms involving S_{yi} . Also note that we put $n = 1$.
3. R. Blinc, M. Ribaric, Phys. Rev. 130, 1816 (1963)
4. R. Blinc, J. Phys. Chem. Solids, 13, 204 (1960)
5. For simplicity we consider only a Bravais lattice of protons.
6. When dipole dipole interactions are included, $\omega(k)$, for small k , depends strongly on the angle between k and the polarisation axis. This effect is restricted, however to a small region of k space near the origin, and can probably not be observed in the present state of the neutron technique.
7. If $J(k)$ is not a maximum for $k = 0$, the material will not be a simple ferroelectric, but will rather choose some more complicated antiferroelectric arrangement below the transition point.
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11. Qualitatively similar, but more complicated expressions would apply if some correlation are retained in the paraelectric phase, as is the case in the Slater model.

On calcule les modes collectifs d'un ensemble de protons dans un cristal du type KH_2PO_4 en tenant compte de l'effet tunnel et d'une interaction simplifiée entre protons. Le spectre de fréquences peut être déterminé par diffusion inélastique des neutrons (par contre, sur les sels deutérés, la bande est étroite et mal couplée aux neutrons). Quand la température s'élève, les fréquences baissent et les modes s'élargissent. Finalement dans l'état paraélectrique on attend un spectre large sur les composés hydrogènes, mais encore étroit (quasi élastique) sur les composés deutérés.