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U Schotte†, M Kabs†§, H Dachs† and K D Schotte‡

† Hahn-Meitner Institut, Glienicker Strasse 100, W-1000 Berlin 39, Federal Republic of Germany
‡ Freie Universität Berlin, Arnimallee 14, W-1000 Berlin 33, Federal Republic of Germany

Abstract. In their high-temperature cubic phase the alkali hydroxides NaOH and KOH and the corresponding deuterated compounds are described by an elastic dipole model for the reorienting OH⁻ groups. The theory describes thermo-diffuse scattering, Huang scattering and phonon softening. The inelastic data and the dispersions of the acoustic modes of KOD are shown and interpreted. Similarities to cooperative Jahn–Teller compounds and alkali cyanides are discussed.

1. Introduction

Recent evaluation of structural data, diffuse x-ray and neutron scattering of NaOH, NaOD and KOH and inelastic neutron scattering of NaOD, all in their cubic high-temperature phases, is contained in a recent paper by Bleif *et al* (1992) (hereafter referred to as I). In this paper the theory used in I for the interpretation of the inelastic neutron scattering and the diffuse x-ray data is explained and in addition applied to the inelastic data for KOD.

The theory is based on a model of pseudo-spin–phonon coupling between reorienting OH groups and harmonic motions of the ions, i.e. the system is looked at as a set of elastic dipoles flipping between discrete orientations in an anisotropic elastic medium. The effect on the acoustic waves is calculated and compared with the measured phonon groups. This model is suggested by the fact that the Debye–Waller factor of the alkali ions is considerably larger than that of the oxygen ions, according to I¶, and by results from quasi-elastic incoherent neutron scattering on NaOH where the reorientational motion of the OH group has been studied by Smith *et al* (1979). In section 2 the details and predictions of the elastic dipole model are discussed. We shall make use of the results obtained earlier when applying this model to the disordered phase of cooperative Jahn–Teller compounds (Graf *et al* 1989, Schotte *et al* 1989).

In section 3 we derive an expression for the inelastic cross section by generalizing the method used by Yamada *et al* (1974) which has the correct limits for $\omega \to \infty$

§ Present address: Heraeus Holding GmbH, W-6450 Hanau 1, Federal Republic of Germany.
¶ For example, for the mean displacements squared, and OH⁻ taken as rigid, one finds that $\langle u_{OH}^2 \rangle / \langle u_K^2 \rangle = 0.6$.

and which is related to thermodiffuse scattering (TDS), and for $\omega \rightarrow 0$ which is the Huang scattering limit. It contains mixing effects between the softened modes which we believe that we have seen in the experimental data. Section 4 is dedicated to the comparison between theory and experiment. Because of the time lapse of more than 10 years since data acquisition this comparison remains more or less qualitative. Its aim is to point out characteristic features in the data.

2. Elastic dipole model for the alkali hydroxides

According to the results of I, NaOH and KOH are in their cubic phases of NaCl structure with O in the Cl sites, and each oxygen can be imagined as surrounded by a cube on which the accompanying proton moves (figure 1). The probability distribution was modelled such that the proton can jump between corner positions or edge middles or both, but the face centres are avoided. According to Smit *et al* (1979) assuming a jump model with eight corner positions or one with rotational jump diffusion, it was found that reorientations take place on a time scale of 10^{-12} s.
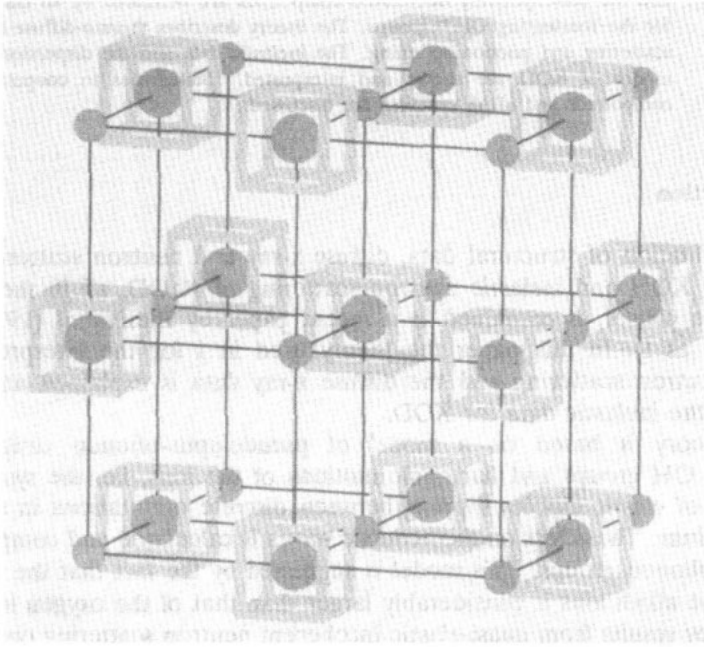

Figure 1. Structure of NaOH and KOH. The shaded cubes indicate the probability distribution of H^+ around the oxygen atom.

We take the OH group as a rigid dumbbell, as is done for the CN group in the alkali cyanides and represent it as an elastic dipole in a certain number of orientations given by symmetry: eight for the corner and 12 for the edge positions. The six face centre positions, although thought improbable, can also easily be treated. The point is to show that, from the acoustic phonon measurements, one can deduce which positions are taken, independently of what was already concluded from the structure data.

We note that the electric dipole moment of OH$^-$ is about three times that of CN$^-$. We still neglected it since we do not expect it to influence the acoustic modes. The optical phonons have not been found in the accessible energy range; they may be totally overdamped owing to the relatively high dipole moment.

The elastic dipole model has proved useful for systems with slower reorientational motions such as CsCuCl$_3$ or K$_2$PbCu(NO$_2$)$_6$ (Mori *et al* 1980) which are cooperative Jahn–Teller compounds, or for the alkali-halide–cyanide glasses (Wochner 1988).

In these systems the shear modes have frequencies in the same range as the molecular jump motions. With inelastic neutron scattering, in 'constant-q scans', one finds a central component at $\omega = 0$ plus 'hard-mode' peaks at high frequencies when the elastic dipoles seem quasi-static. With smaller wavevectors, overdamped and 'soft modes' are seen. The latter sets in when the dipoles move so fast that a new effectively softer medium is seen by the neutrons. As described in I, for the plastic modification of NaOH (NaOD) we concluded that, in a similar way, as for the pure cyanides (Rowe *et al* 1975, 1978), the soft-to-overdamped region cannot be left up to the zone boundary for the c_{44} and c'' shear modes, because the dipoles move faster by an order of magnitude. Therefore the model of local perturbers in a 'hard elastic' medium seems somewhat artificial. We recall, however, that vice versa the soft-c_{44}-mode regime in CsCuCl$_3$ could not be reached since it was expected for inaccessibly small q; the soft shear constant was only known from ultrasonic measurements but could be predicted from the theory used for the inelastic neutron scattering data.

We proceed to write down the free energy of the elastic dipole system embedded in an elastic medium of cubic symmetry. It is formally the same as has been used before (Schotte *et al* 1989). The elastic dipole is a 3×3 tensor in a simple approximation expressed by

$$P_{ij} = d_i d_j - (d^2/3)\delta_{ij} \tag{1}$$

where d is one of the eight $\langle 111 \rangle$ or one of the 12 $\langle 110 \rangle$ directions which we later distinguish by the index r. An as yet unknown strength factor is thought to be incorporated in d.

The simple form of (1) is correct for an isotropic medium and the $\langle 111 \rangle$ direction in the cubic system. In general the elastic medium reacts to the local distortion such that individual components of P are proportional to 'effective' shear constants. This is treated by Schotte *et al* for the hexagonal medium. The corresponding modification needed here is given below. It does not change the outcome of the following discussion. (In fact, equation (1) is not even general enough to describe the simplest 'volume dipole' with $P_{xx} = P_{yy} = P_{zz}$ and the other components zero.) In an elastic medium, as a first approximation, one assumes a linear coupling to the deformations. The elastic energy is then given by

$$H = \tfrac{1}{2}\sum_{ijkl} \lambda_{ijkl}\epsilon_{ij}\epsilon_{kl} + \sum_{rnij} P_{ij}^r \epsilon_{ij} c^r(R_n) \tag{2}$$

where λ_{ijkl} are the elastic constants,

$$\epsilon_{ij} = \tfrac{1}{2}(\partial u_i/\partial x_j - \partial u_j/\partial x_i) \tag{3}$$

and $c^r(R_n) = 1$ if there is an elastic dipole of type r in location R_n and $c^r(R_n) = 0$ if not. After Fourier transformation and expansion of the displacements u_i in normal

acoustic modes, introducing the Fourier transform of the concentration fluctuation $c^r(R_n) - c$ as (pseudo-)spin $c^r(q)$, the interaction term is

$$H_{sp} = \sum_{qjr} i(\mathbf{P}^r q \cdot e_j) Q_j(q) c^r(-q) \tag{4}$$

where e_j is the normalized polarization vector of a mode $\omega_j(q)$ and wavevector q and $Q_i(q)$ is the phonon amplitude or normal coordinate.

We shall use $\omega_i^2 = c_{ii} q^2/\rho$ where ρ is the density and c_{ii} is the elastic constant or combination of elastic constants.

The free energy can now be written as (leaving out the obvious dependence on q)

$$F = \tfrac{1}{2} \sum_{qj} (p_j p_j^* + \omega_j^2 Q_j Q_j^*) + \sum_{qjr} [h_j^r c^r(q) Q_j^* + \text{cc}] + \frac{r_0 kT}{2} \sum_{q,r} c^r(q) c^r(-q) \tag{5}$$

where r_0 is the number of dipole directions, p_j are the momenta and the last term is the entropy term TS. F can be minimized with respect to the spin by putting $\partial F/\partial c^r = 0$, solving for c^r and inserting back into (5) to obtain an effective phonon energy

$$F_{phon} = \tfrac{1}{2} \sum_{qj} \Omega_j^2(q) Q_j Q_j^* \tag{6}$$

with

$$\Omega_j^2(q) = \omega_j^2(q) - \frac{1}{r_0} \sum_r \frac{|h_j^r|^2}{kT}. \tag{7}$$

We shall use

$$h_j^2 \equiv \sum_r |h_j^r|^2 = \sum_r (\mathbf{P}^r q \cdot e_j)^2 \tag{8}$$

or, with (1),

$$h_j^2 = \sum_r |(d^r \cdot e_j)(d^r \cdot q) - \frac{d^2}{3}(q \cdot e_j)|^2. \tag{9}$$

Ω_j in (7) will be called for short the softened mode and ω_j the hard mode.

In (7), $\sum_r h_i^r h_j^r = 0$ for $i \neq j$ has been used, which results from the symmetry properties of the $\mathbf{P}^r$ tensors.

For the cases of practical interest we calculated h_i^2/r_0 from (9) for the three types of dipole:

$$d_R = \sqrt{\alpha}\langle 111\rangle \qquad d_K = \sqrt{3\alpha/2}\langle 110\rangle \qquad d_F = \sqrt{3\alpha}\langle 100\rangle \tag{10}$$

using the wavevectors and polarizations given on the left-hand side in table 1. The angular brackets denote the symmetrically equivalent set of eight corner, 12 edge and six face centre positions of H^+ (or D^+).

The results in table 1 on the right-hand side tell us that neither the eight-corner nor the six-face-centre model will do since then either c_{44} or c'' would not soften (they do soften that we already know from NaOD). The edge model effects all modes;

Table 1.

Wavevector	Polarization	Elastic constant	$h_i^2(d_F)/6$	$\frac{1}{8}h_i^2(d_R)$	$\frac{1}{12}h_i^2(d_K)$
$q=(q_x,0,0)$	$e_1(1,0,0)$	c_{11}	$2\alpha^2 q_x^2$	0	$\frac{1}{2}\alpha^2 q_x^2$
	$\left.\begin{array}{l} e_2=(0,1,0) \\ e_3=(0,0,1) \end{array}\right\}$	c_{44}	0	$\alpha^2 q_x^2$	$\frac{3}{4}\alpha^2 q_x^2$
$q=(q/\sqrt{2})(1,1,0)$	$e_1=(1/\sqrt{2})(1,1,0)$	$c'=\frac{1}{2}(c_{11}+c_{12})+c_{44}$	$\frac{1}{2}\alpha^2 q^2$	$\alpha^2 q^2$	$\frac{7}{8}\alpha^2 q^2$
	$e_2=(1/\sqrt{2})(1,-1,0)$	$c''=\frac{1}{2}(c_{11}-c_{12})$	$\frac{3}{2}\alpha^2 q^2$	0	$\frac{3}{8}\alpha^2 q^2$
	$e_3=(0,0,1)$	c_{44}	0	$\alpha^2 q^2$	$\frac{3}{4}\alpha^2 q^2$
$q=(q/\sqrt{3})(1,1,1)$	$e_1=(1/\sqrt{3})(1,1,1)$	$\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$	0	$\frac{4}{3}\alpha^2 q^2$	$\alpha^2 q^2$
	$\left.\begin{array}{l} e_2=(1\sqrt{6})(-2,1,1) \\ e_3=(1/\sqrt{2})(0,-1,1) \end{array}\right\}$	$\frac{1}{3}(c_{11}-c_{12}-c_{44})$	$\alpha^2 q^2$	$\frac{1}{3}\alpha^2 q^2$	$\frac{1}{2}\alpha^2 q^2$

however, the softening effects on c'' and c_{44} are comparable only, if we admit *all* three kinds of OH orientation.

Nothing has been said yet about the strength of the elastic dipoles in the symmetrically different directions. Following the ideas of Khatchaturian (1966), an elastic dipole takes in a small volume V in the elastic medium inside which there is no internal stress; that is, with the elastic energy and one dipole in r_0,

$$H = \sum \left(\tfrac{1}{2}\lambda_{ijkl}\epsilon_{ij}\epsilon_{kl} + \frac{\epsilon_{ij}P_{ij}\theta(r-r_0)}{V} \right) \tag{11}$$

where $\theta = 1$ for r within the volume around r_0 and zero for r outside, one has the condition

$$\left. \frac{\partial H}{\partial \epsilon_{ij}} \right|_{\text{(ins)}} = 0 = \frac{P_{ij}}{V} + \sum_{kl}\lambda_{ijkl}\epsilon_{kl}^{(\text{ins})}. \tag{12}$$

The deformation $\epsilon_{kl}^{(\text{ins})}$ (inside V) follows from crystal geometry and (1) can be used to calculate it. From (11), one determines the shape of P_{ij} for an anisotropic medium; for example, for the deformation along $d_K = (1/\sqrt{2})(1,1,0)$, one finds in the cubic system that

$$\mathbf{P}_K = -\alpha V \left(\frac{c''}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + c_{44} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right). \tag{13}$$

The first tensor in (13) would describe the dipole $\mathbf{P}_F$ in the $(0,0,1)$ direction. For d_R in one of the $\langle 111 \rangle$ directions, $\mathbf{P}_R$ stays homogeneous and is proportional to c_{44}. For example, for ϵ_{ij} from a distortion along $d_R = (-1,1,1)/\sqrt{3}$,

$$\mathbf{P}_R = -\frac{2}{3}c_{44}\frac{\alpha}{V} \begin{pmatrix} 0 & -1 & -1 \\ -1 & 0 & 1 \\ -1 & 1 & 0 \end{pmatrix}. \tag{14}$$

For plastic crystals it is not clear which elastic constants should be used here and α is not known either. There may be a chance to estimate it from the Debye–Waller factor. We just note that the three types of dipole have in principle different strengths owing to the 'anisotropic reaction' of the medium. We consider c'' and c_{44} to be of roughly the same order of magnitude and use the results in table 1 as a guideline as far as possible.

3. Inelastic cross section of a pseudo-spin–phonon coupled system

We start with the simplified expression for the inelastic neutron scattering cross section, depending on neutron energy transfer ω and K, the scattering vector:

$$\frac{d^2\sigma}{d\omega\,d\Omega} = b^2 \sum_i (K \cdot e_i)(K \cdot e_i)\langle Q_i Q_i \rangle \tag{15}$$

where $e_i \equiv e_i(q)$ is a polarization of the wave with wavevector q and $K = G + q$ with G a Bragg reflection, b is the scattering length which contains the elastic structure

factor and the Debye–Waller factor and $d\Omega$ is the element of solid angle. We wish to calculate $\langle Q_i Q_i \rangle$ as a function of energy transfer ω and wavevector q. For the model to be used, $\langle Q_i Q_j \rangle = 0$ for $i \neq j$ which will be easy to see below. Following Yamada *et al* (1974) (see also the textbook by Landau and Lifschitz (1966)), it is helpful to consider a set of time-dependent correlation functions

$$\Phi_{ij}(t) = \langle x_i(t) x_j(0) \rangle \tag{16}$$

where x_i refers to the components of a state vector, e.g. for a system with one phonon and one pseudo-spin $x = (p, Q, S)$ with momentum p, normal coordinate Q and spin variable S. The average refers to a Gaussian average determined by $\frac{1}{2}\beta_{ij} x_i x_j$ in the exponent which is related to the Gibbs enthalpy $H = E - TS$. For example, with a linear coupling between phonon and spin,

$$(kT/2)\beta_{ij} x_i x_j = p^2/2 + \omega_0^2 Q^2/2 + hQS + kTS^2/2 \tag{17}$$

so that the matrix for β_{ij} is given by

$$\beta = \frac{1}{kT} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \omega_0^2 & h \\ 0 & h & kT \end{pmatrix}. \tag{17'}$$

The Fourier–Laplace transform

$$\tilde{\Phi}_{ij}(\omega) = \int_0^\infty \langle x_i(t) x_j(0) \rangle \exp(\mathrm{i}\omega t)\, \mathrm{d}t \tag{18}$$

can be expanded asymptotically:

$$\tilde{\Phi}_{ij}(\omega) = -\Phi_{ij}(0)/\mathrm{i}\omega - \dot{\Phi}_{ij}(0)/\omega^2 - \dots. \tag{19}$$

The equal time average is given by

$$\Phi_{ij}(0) = (\beta^{-1})_{ij} \tag{20}$$

which is the ij component of the inverse of the matrix β. The next term is determined by a matrix γ which contains information about the dynamics:

$$\dot{\Phi}(0) = -\gamma = - \begin{pmatrix} 0 & kT & 0 \\ -kT & 0 & 0 \\ 0 & 0 & \gamma \end{pmatrix}. \tag{21}$$

The crucial difficulty when applying this procedure to the spin–phonon problem lies in the equation of motion for the spin. The spin is taken as a relaxator with a flip rate γ. The definition of γ implies that

$$\dot{x}_i = -(\gamma\beta)_{ij} x_j \tag{22}$$

so that the mean value of the dissipation

$$\frac{\mathrm{d}}{\mathrm{d}t} H = kT \sum_{ij} \langle \dot{x}_i x_j \rangle \beta_{ij} = -kT \sum (\gamma^{-1})_{ij} \langle \dot{x}_i \dot{x}_j \rangle = -kT \frac{\dot{S}^2}{\gamma} \tag{23}$$

comes from the frictional forces acting on the pseudo-spin alone.

· The asymptotic form for the correlation function is not very useful. A rational (in the mathematical sense) approximation, sometimes called the Padé approximation, having the same asymptotic form is

$$\tilde{\Phi}(\omega) = \beta^{-1}[1/(i\omega\beta^{-1} - \gamma)]\beta^{-1}. \tag{24}$$

According to the definition of the state vector we need the (2,2) element of this matrix. After some matrix algebra, one obtains, with (17) and (21),

$$\tilde{\Phi}_{22}(\omega) = \frac{kT}{\gamma(\omega_0^2 - h^2/kT)} \frac{h^2 kT + i\omega(\gamma + i\omega)}{\omega_0^2 - \omega^2 - h^2/kT + (i\omega/\gamma)(\omega_0^2 - \omega^2)}. \tag{25}$$

For (15), one needs the Fourier transform of (16). Since $\Phi_{22}(t)$ is an even function in time, one has

$$\langle QQ \rangle_\omega = \frac{1}{\pi} \operatorname{Re} \tilde{\Phi}_{22}(\omega) = \frac{kT}{\pi\gamma} \frac{h^2/kT}{(\omega^2 - \omega_0^2 + h^2/kT)^2 + (\omega^2/\gamma^2)(\omega^2 - \omega_0^2)^2}. \tag{26}$$

If we take this as $\langle Q_i Q_i \rangle$ referring to one of three acoustic modes, then $\langle Q_i Q_j \rangle$ ($i \not= j$) would be proportional to $h_i h_j$ which is zero for symmetry reasons if one uses (8) or (9). We note that diffuse x-ray scattering giving TDS is determined to a good approximation by the integral over ω in (15). The integral to be calculated is of the form

$$\int_{-\infty}^{\infty} \langle QQ \rangle_\omega \, d\omega = \int_{-\infty}^{\infty} \tfrac{1}{2}[G^+(\omega) + G^-(\omega)] \, d\omega \tag{27}$$

with G^+ analytic in the upper half-plane and G^- in the lower half. Obviously the integrand decreases sufficiently rapidly for large ω for the theorem from functional theory to be used:

$$G^{\pm}(\omega) = \pm\frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{\langle QQ \rangle_w \, dw}{w - \omega \mp i\eta} \tag{28}$$

and

$$\lim_{\omega \to \infty} G^{\pm}(\omega) = \frac{1}{\pi i \omega} \int_{-\infty}^{\infty} \langle QQ \rangle_w \, dw. \tag{29}$$

This means that one needs only the residuum at $\omega = \infty$, i.e. $(\beta^{-1})_{22}$ with (19) and (20) which can be found from (17). Therefore the TDS does not depend on assumptions about the dynamics but is solely determined by the softened mode:

$$\int_{-\infty}^{\infty} \langle QQ \rangle_\omega \, d\omega = \frac{kT}{\omega_0^2 - h^2/kT}. \tag{30}$$

In principle, one could measure elastic constants and follow softening near phase transitions in diffuse x-ray scattering. The rare occasion where this has been achieved quantitatively is for NaOH (ordered phases) by Bleif (1978).

It is straighforward to extend (17) to the general case for all acoustic modes and an r_0 component spin (equations (5)–(7)) so that

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{TDS}} = b^2 kT \sum_i \frac{(K \cdot e_i)^2}{\Omega_i^2} = b^2 kT(K \cdot D_s^{-1} K) \tag{31}$$

where $\mathbf{D}_s^{-1}$ is the inverse of the elastic matrix with Ω_i^2 as eigenvalues and e_i as eigenvectors. For the inelastic cross section, the mathematical method is straightforward; however, the strategy with respect to the relaxation process is unclear. If each spin component relaxes only within itself, $\dot{S}^r \sim -\gamma S^r$, all modes are decoupled and one obtains an expression such as (26) for each mode with h_i^2 from (8). This would result in an expression for Huang scattering at $\omega \simeq 0$ which can be checked against the experimental results for CsCuCl$_3$:

$$\left.\frac{d^2\sigma}{d\omega\,dq}\right|_{\omega=0} = \frac{b^2}{\pi\gamma}\sum_i (\boldsymbol{K}\cdot\boldsymbol{e}_i)^2 \frac{h_i^2}{\Omega_i^4} = \frac{b^2}{\pi\gamma}\sum_r |\boldsymbol{K}\cdot\mathbf{D}_s^{-1}\mathbf{P}^r q|^2 \tag{32}$$

which looks like the usual result but with 'softened' elastic constants. From a concept viewpoint, and as confirmed by the experimental findings, it makes little sense to use the 'soft' elastic constants in Huang scattering (Schotte 1987). From the experiments, one rather expects a result such as (32) with 'hard' elastic constants. The temperature may enter via a susceptibility. We have pursued such an approach for CsCuCl$_3$, extending it to three phonons for each q and sticking to a single relaxation time (Schotte *et al* 1989). The expression found for the inelastic cross section described the mixing effects well and also gave the desired form for Huang scattering except that the susceptibility had a dependence on the direction of the wavevector which distorted the Huang isointensity contours not much but noticeably at T close to the phase transition. Also the TDS limit was only given up to higher-order terms in h_i^2, and the case of degenerate modes was not treated well; for example the soft c_{44}^s measured along $q = (1,0,0)$ would have been different from that with $q = (1,1,0)$ (see table 1 for degeneracy).

We shall not repeat this earlier version but give the improved version which follows by adding higher-order terms in the denominator in h_i^4 and h_i^6. It now has the expected limit for $\omega \to \infty$ (TDS) and a reasonable Huang limit. In the improved form the phonon correlation function is given by

$$\langle Q_1 Q_1 \rangle = \frac{kT}{\pi\gamma} \frac{h_1^2(q)(\omega^2 - \omega_2^2)^2(\omega^2 - \omega_3^2)^2}{r_0 kT}$$

$$\left/\left[\prod_i \left(\omega^2 - \omega_i^2 + \frac{h_i^2(q)}{r_0 kT}\right)^2 + \frac{\omega^2}{\gamma^2}\prod_i(\omega^2 - \omega_i^2)^2\right]\right. \tag{33}$$

The products in the square brackets refer to the three modes for each q. We repeat that this expression is identical with that derived earlier up to higher-order terms in h_i^2 in the products. We leave the reader to show that we achieved this by putting

$$x_1 x_2 x_3 - a_1 x_2 x_3 - x_1 a_2 x_3 - x_1 x_2 a_3 \simeq (x_1 - a_1)(x_2 - a_2)(x_3 - a_3)$$

where

$$x_i = \omega^2 - \omega_i^2$$

and

$$a_i = h_i^2/r_0 kT.$$

The LHS is in the earlier version and the RHS is the first product in (33).

The main purpose of the first part of this section was to show that we use essentially a Padé approximation which gives the pole structure reliably (phonon peaks) but not necessarily the $\omega \to 0$ limit (Huang scattering). We therefore find a modification justified which has the expected pole structure (soft and hard modes, and degeneracy treated correctly), gives the correct TDS limit and improves on the Huang limit.

The Huang limit can now be written as

$$\left.\frac{\mathrm{d}^2\sigma}{\mathrm{d}\omega\,\mathrm{d}\Omega}\right|_{\omega=0} = b^2 \sum_r |\boldsymbol{K} \cdot \mathbf{D}^{-1}\mathbf{P}^r q|^2 \left|\frac{\det D}{\det D_s}\right|^2 = I_{\text{Huang}} \prod_i \frac{1}{(1 - h_i^2/\omega_i^2 r_0 kT)^2}. \quad (34)$$

It has been checked that the quasi-elastic scattering of $CsCuCl_3$ ($\omega \simeq 0$) is now well described (Graf 1992). We also checked the full width at half-maximum (FWHM) as in the work of Schotte (1987), for its dependence on the elastic constants. There is almost no difference between the FWHM from (34) and that from the bare I_{HUANG}, but (32) disagrees with the experimental result.

We shall, in the next section, evaluate the scattering cross section resulting from (33) for the experimental data available.

4. Experimental results and application of theory

The neutron scattering data available for NaOD are to be found in I. Some will be reproduced to make sure of the theoretical description since the KOD data are in a way less complete and the behaviour is expected to be similar. The measurements were performed at the IN2 instrument of the Grenoble high-flux reactor (Kabs 1982); for details see I.

Since the temperature span of the cubic phase is much larger for KOD than for NaOD (NaOD, from 561 to 593 K; KOD, from 513 to 678 K), the temperature dependence of the phonon softening might have been detected. For KOD, inelastic scattering was measured for 573 and 623 K, but this temperature difference is estimated to lead to a change in the soft elastic constant within the accuracy of the determination of the elastic constants (about 5%); so at this point there is no chance to check the theory.
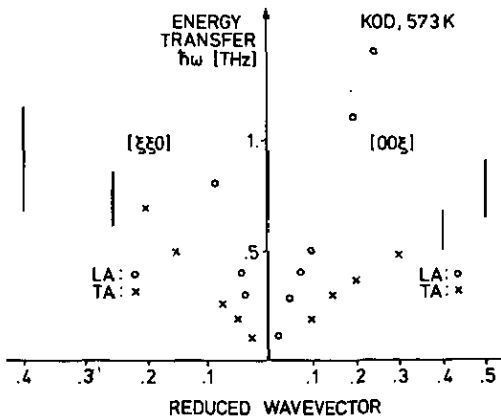

Figure 2. Dispersions of the acoustic modes for KOD relating to c_{44} along $[00\xi]$ (TA mode), c_{11} along $[00\xi]$ (LA mode), c' along $[\xi\xi0]$ (LA mode) and c'' along $[\xi\xi0]$ (TA mode), as deduced from the experiments with overdamping.

Figure 2 shows the experimental results evaluated to give dispersions for the acoustic modes, with the start of overdamping indicated. The steep longitudinal branches were difficult to pursue owing to a lack of intensity. The corresponding elastic constants (see also table 1) are listed in table 2. According to the theory they are the softened values.

Table 2. Elastic constants (from experiment).

Elastic constant (units)	NaOD	KOD
c_{11} (10^{10} dyn cm^{-2})	21.5	18.6
c_{44} (10^{10} dyn cm^{-2})	4.4	2.5
$c' = \frac{1}{2}(c_{11} + c_{12} + 2c_{44})$ (10^{10} dyn cm^{-2})	25.2	16.8
$c'' = \frac{1}{2}(c_{11} - c_{12})$ (10^{10} dyn cm^{-2})	1.6	4.2

With the values in table 2 the TDS isocontours in q-space have been calculated and a reasonable resemblance to the x-ray result was found for NaOH, in I; in particular, the 'diffuse streaks' could be explained as caused by the very small values of c_{44} and c''. Note that the anisotropy $(c_{11} - c_{12} - 2c_{44})/c_{44}$ has different signs for NaOD and KOD from which characteristic differences also in the diffuse scattering can be predicted (there is, however, no such measurement for KOD). By choosing $K = 020$ and 220 for $q = (1, 1, 0)$ and $(\pm 1, 1, 0)$, appropriate single modes are picked out. Therefore, (33) is representative of the scattering cross section. In principle it contains seven parameters (at most). The three softened elastic constants will be used in the linear dispersions, e.g.

$$\Omega_{11} = \sqrt{c_{11}/\varrho}(2\pi/a)q \qquad 0 \leqslant q \leqslant 0.5 \qquad (35)$$

with $\rho = 2$ g cm^{-3}, $a = 5.7$ Å for KOD and 5.1 Å for NaOD. For the 'hard' modes, somewhat larger values are tried but of course not quite arbitrarily and using table 1. For γ one starts out with the experimental value of around 0.5 THz (Smit *et al* 1979). It could be smaller because of the higher D$^+$ mass; it could be larger because D$^+$ should be distributed over more than eight sites as assumed by Smith *et al* . The final result which appears to give a good description of the experiment is surprising; it is not possible to use a single flip rate. We could do with two flip rates: a slow rate where the edge and face centre dipoles are involved (c_{11} and c'') and a faster rate where the corner dipoles dominate (c_{44} and c') (see table 1). The fitted factor of 3 between them is plausible if we remember from the structure data in I that the probability distribution of the proton is smaller by a factor of about 4 for the face centres than for the corners of the cube around the oxygen atom.

Also γ is 30% lower for NaOD than for KOD which again is plausible since the K ions are farther apart and the D$^+$ motions less impeded. The c' mode is the only one (measurable in the chosen experimental set-up) which is influenced by all three dipoles and is expected to be connected to an even higher flip rate. However, no relevant experimental data focusing on this LA mode have become available so far.

In table 2 the starting parameters used for the computer simulations are listed. The simulations lead to the values in table 3. Before we discuss them, let us look at the neutron scattering data and the theoretical simulations.

In figures 3–6, original data together with calculations from (33) are shown. The c_{44} and c'' phonon groups show the expected softening and damping behaviour with

Table 3. Elastic constants ('soft' from experiment and 'hard' from theory fit) and also the flip rates γ from fitting.

Elastic constant (units)	NaOD	KOD
c_{11}, soft (10^{10} dyn cm^{-2})	21.5	18.6
c_{11}, hard (10^{10} dyn cm^{-2})	30.4	21.3
γ (THz)	0.15	0.21
c_{44}, soft (10^{10} dyn cm^{-2})	4.4	2.5
c_{44}, hard (10^{10} dyn cm^{-2})	7.6	4.4
γ (THz)	0.45	0.64
c'', soft (10^{10} dyn cm^{-2})	1.6	4.2
c'', hard (10^{10} dyn cm^{-2})	8.25	6.2
γ (THz)	0.15	0.21
c', soft (10^{10} dyn cm^{-2})	25.2	16.8
c', hard (10^{10} dyn cm^{-2})	29.7	19.54
γ (THz)	0.45	0.64
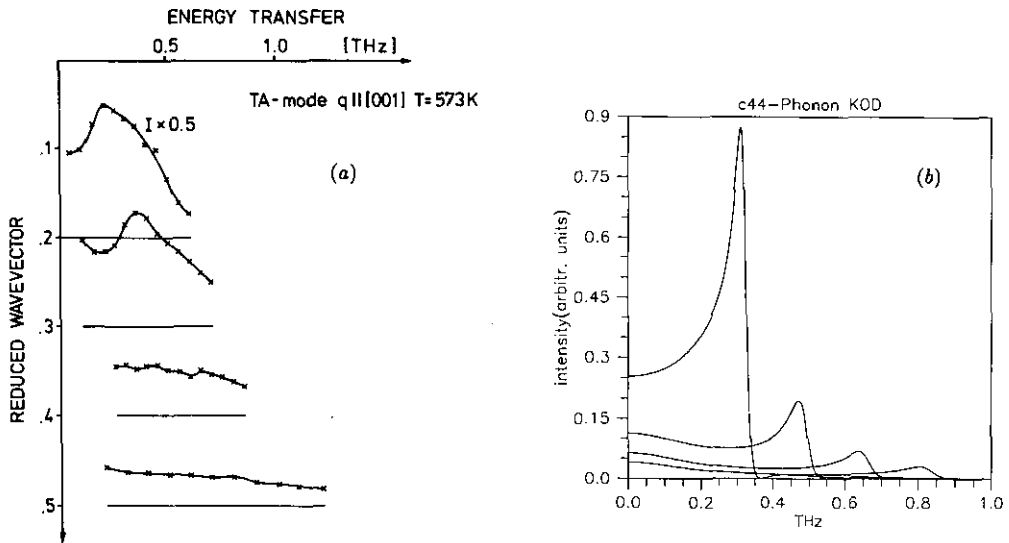
Figure 3. (*a*) Original data from inelastic neutron scattering for KOD: constant-q scans for the c_{44} shear mode. The lines are guides to the eye, and also in the following figures. (*b*) Theoretical simulation, using (33) and table 3, of c_{44} phonon groups of KOD. The same q-values as in the experiments are used.

the development of the central component as expected. One might think that for this the original formula of Yamada *et al*, i.e. equation (26), would have been sufficient. From figure 7 for the c_{11} phonon of NaOD, we can see that the full expression (33) is necessary; compare figures 7(*a*) and 7(*b*). In figure 7(*c*) the 'single-mode softening' is plotted, which does not reproduce the experimental findings. The mixing effects contained in (33) and figure 7(*b*) also subtract the intensity from the $\Omega(c_{11})$ peaks and therefore make the dispersion difficult to follow up to higher q. Note that $\langle Q_1 Q_1 \rangle$ (equation (33)) has zeros at ω_2 and ω_3, which leads to the fine structure in figure 4(*b*), when Ω_1 and ω_2 (or ω_3) are close. It is not clear whether this is contained in the experimental data or an artefact of the theory (in practice these zeros are just dips if
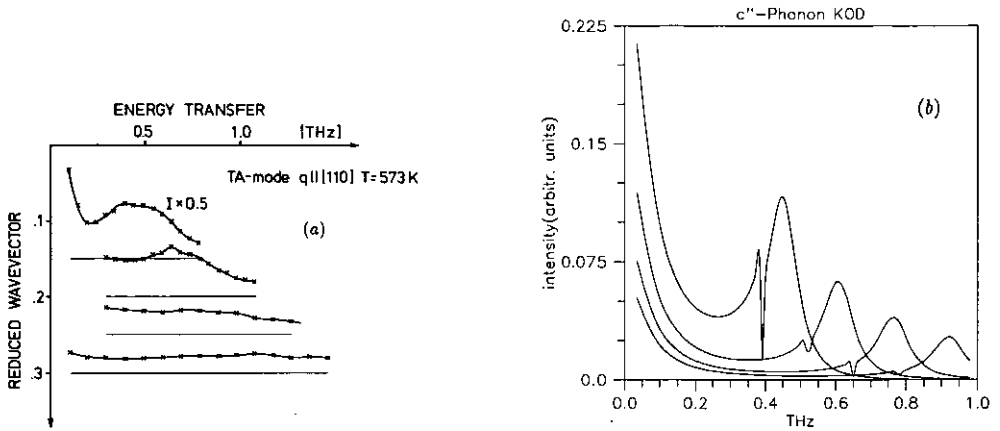
Figure 4. (a) Experimental data for the c'' shear mode of KOD. (b) Theoretical simulation of the c'' phonon groups, as for figure 3(b); and again for the same q-values as for (a).
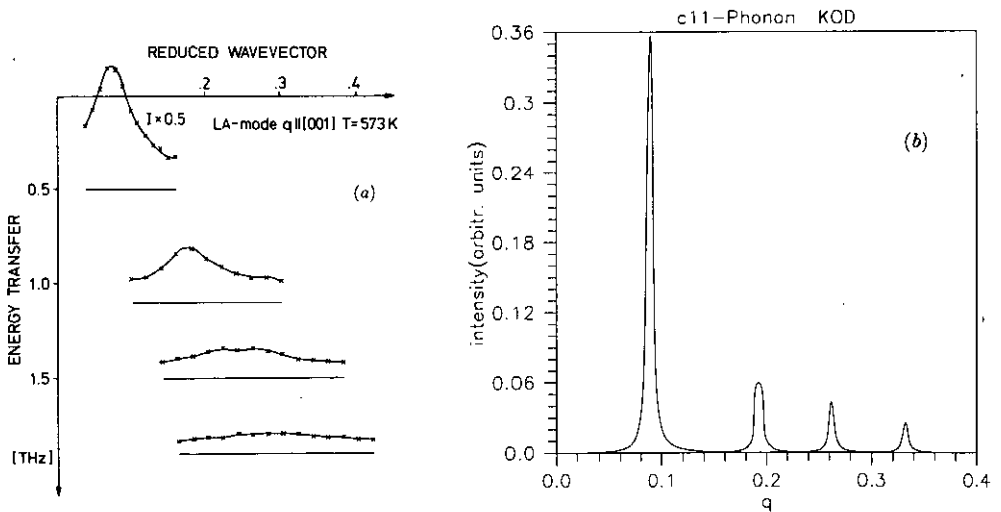

Figure 5. (a) Constant-energy scans for the c_{11} LA mode of KOD. (b) Simulation of the results in (a), using the same ω-parameters; see ordinate of (a). Four single-peak curves are depicted.

one assumes a 'natural' linewidth for the hard modes). Figure 5 is a constant-E scan for the c_{11} mode of KOD. Unfortunately the corresponding simulations are not very informative; there are always peaks given by $\Omega(c_{11})$ and they become somewhat wider or higher if one changes γ or the hard c_{ij}-values. From them it is not possible to obtain the parameters as in table 3. The same holds for the c' mode and constant-E scan shown in figure 6.

Returning to the parameters in table 3, the fitted values lead to the conclusion that all contributions, i.e. the last three columns in table 1, count. One sees from
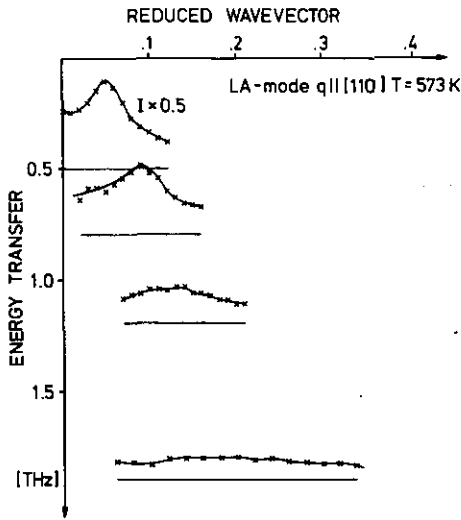
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Figure 6. Constant-energy scans for the c' LA mode. The simulation from theory is tedious; see text.

table 3 that for KOD the softening contributions $c_{44}^0 - c_{44}^s$ and $c_0'' - c_s''$ are comparable; the same holds for c_0' and c_{11}^0 and there is a difference between them of a factor of about $3/2$ as suggested by table 1.

NaOD at first glance seems to behave strangely; in particular, the softening of c'' is extreme. Returning therefore to the idea of the anisotropy of the dipole tensors (end of section 2) we used (12)–(14) to calculate the dependence of the shear modes of all contributions in table 1. The result is, summing the contributions from d_R, d_F and d_K,

$$c_{11}^s = c_{11}^0 - \tfrac{10}{3}(c'')^2 a(T) \qquad c_s'' = c_0'' - \tfrac{5}{2}(c'')^2 a(T)$$
$$c_{44}^s = c_{44}^0 - \tfrac{7}{3}(c_{44})^2 a(T) \qquad c_s' = c_0' - [\tfrac{7}{3}(c_{44})^2 + \tfrac{5}{6}(c'')^2]a(T) \tag{36}$$

with $a(T) = \alpha^2/V^2 kT$.

Even with $a(T)$ unknown, one can see that, if c'' is larger than c_{44} by a factor of about 1.4 (which does not seem unreasonable), the values for NaOD in table 3 are consistent and again strongly support the suspicion that all the dipole types are necessary to describe the phonon behaviour. While this could be taken as an indication that the H^+ (or D^+) move basically on a sphere, we recall that the dipoles have different strengths, which should (or must according to our findings) be contained in the probability distribution and thereby the jump rates between the different types of H^+ and/or D^+ positions.

5. Conclusions

In their cubic phases, NaOH and KOH are plastic crystals. The internal reorientational motions are so fast that, in inelastic neutron scattering, only softened and overdamped acoustic modes are seen. We developed a theoretical description based on the concept of flipping elastic dipoles. It contains the mixing effects of softening modes, which are visible in the experimental data, and describes TDS as found from quasi-static diffuse x-ray scattering. For $\omega = 0$, the Huang limit has been
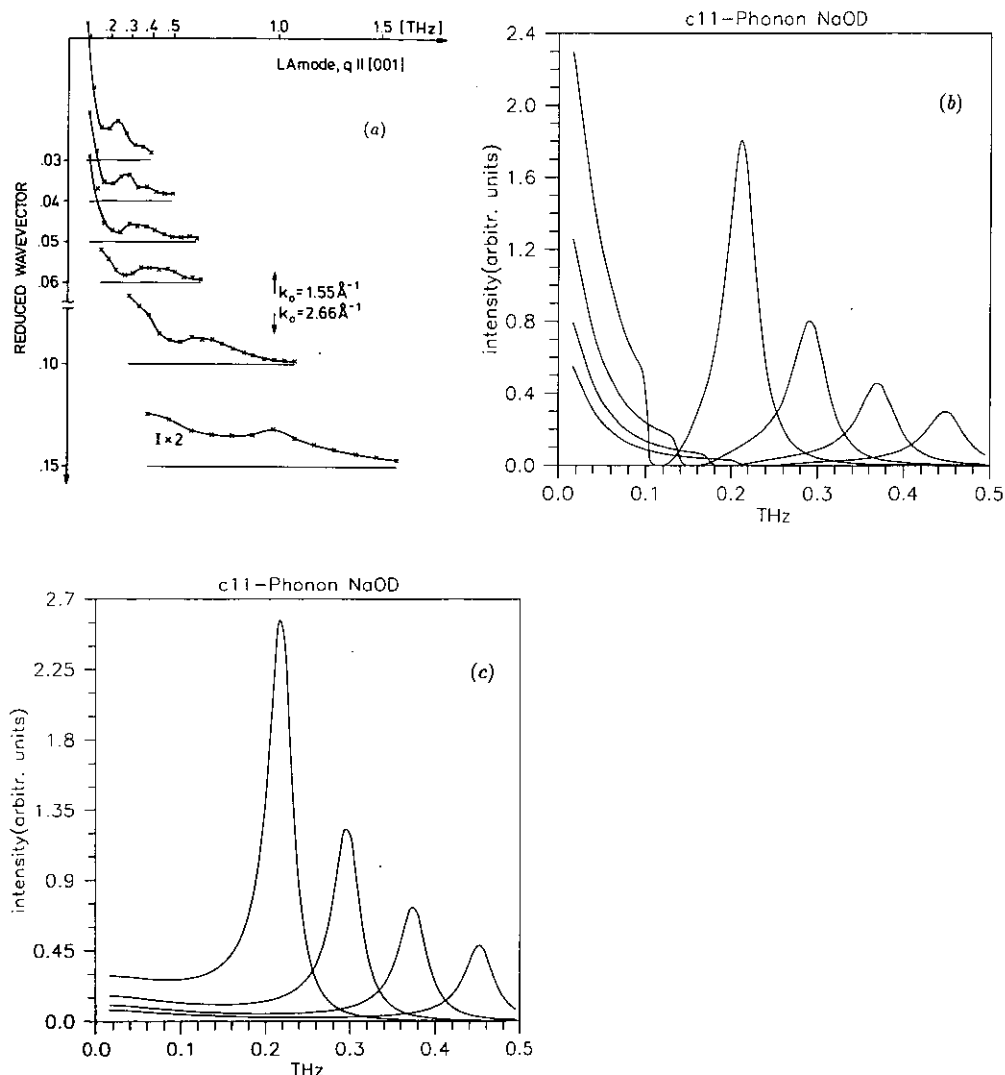
Figure 7. (*a*) Original data for the c_{11} LA mode of NaOD. (*b*) Simulation of the c_{11} phonon groups with the full phonon correlation function (33), showing mixing effects. (*c*) Simulation with the one-phonon correlation function (26), note the absence of mixing effects.

checked for $CsCuCl_3$, since the hydroxides in principle cannot show Huang scattering for which the reorientational motion of OH must be slower than the lattice motions.

The basic results from interpreting the neutron data with this theory are, firstly, that the symmetrically different types of dipole for corner, edge and face centre positions of H^+ couple to different acoustic modes and show differing flip rates and, secondly, that also the face centre dipoles, thought to be less probable from the structure data, play a role in phonon softening and are responsible for much of the strong softening of the c'' mode in NaOD. Thus the protons probably move on a sphere around the oxygen atom with strongly anisotropic residence times in the symmetrically different positions relevant to phonon softening. KOD seems more

isotropic (i.e. the dipoles have very similar strengths in the different directions) and the OD groups have higher (30%) flip rates, which seems plausible in the wider lattice.

Acknowledgments

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