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A neutron scattering study of the dynamics in a $K(D_xH_{1-x})_2PO_4$ system

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Abstract. An investigation of the relatively low-frequency (28 meV = 7 THz) motion of protons in KH_2PO_4 (KDP) has been carried out using time-of-flight (TOF) neutron spectroscopy. A study of the relevant coherent response from single-crystal KD_2PO_4 (DKDP) has also been undertaken. Regarding the incoherent inelastic peak in KDP, the temperature dependences of the excitation energy, the energy width and the intensity were measured. The same measurements were carried out on a 90% deuterated sample. Strong damping of the peak in the paraelectric phase was observed for both samples, while the peak position was nearly temperature independent. Moreover, the temperature variation of the thermal parameter for the proton exhibited a marked discontinuity at T_c. It has been revealed by a coherent-scattering measurement around the (303) and (503) zones that this mode has a collective nature with energy dispersion in DKDP, and that it also shows strong damping in the paraelectric phase. The results suggest that the mode couples to the fluctuation of dipole moments, and that the fluctuation can possibly be described in terms of the order–disorder model.

1. Introduction

The role of protons in the ferroelectric phase transitions in KDP- (KH_2PO_4)-type hydrogen-bonded crystals is not yet fully understood. Since there is a large isotope effect on the transition temperature (T_c for KDP is 122 K and for DKDP (KD_2PO_4) it is 220 K), the behaviour of the protons or the deuterons has especially been noted (Slater 1941, Blinc 1960, de Gennes 1963, Tokunaga and Matsubara 1966). A widely accepted theoretical model for the transition in KDP is that proposed by Kobayashi (1968), in which coupling between an optic phonon and a collective motion of protons along the hydrogen bond is assumed. However, the proton system alone cannot account for the ferroelectric phase transition, since the assumed protonic motion is within the *ab* plane (the direction of the hydrogen bond is perpendicular to the *c* axis), while the ferroelectric polarization is parallel to the *c* axis. In the Kobayashi model the cooperative proton ordering (or localization) in a double-well potential along the hydrogen bonds was assumed to cause a softening of the coupled optic phonon. The large isotope effect has been explained by introducing a tunnelling motion of the protons, which hinders the localization into one of two equilibrium positions along the hydrogen bond.

Experimentally, a prominent feature is the existence of a heavily damped low-frequency response in the Raman scattering spectra (Kaminow and Damen 1968). The Raman spectra were analysed as demonstrating a soft ferroelectric mode, and the corresponding

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characteristic frequency was determined. The mode becomes underdamped under high pressure (Peercy 1975). Neutron quasi-elastic scattering experiments (Paul *et al* 1970, Skalyo *et al* 1970) on DKDP have also shown a temperature-dependent heavily damped mode. A study of phonons in single-crystal DKDP by Paul *et al* (1970) could not find any underdamped optic mode in which the frequency tends to zero as the ferroelectric transition is approached. Recent studies of the infrared reflectivity of KDP (Wyncke and Bréhat 1986), DKDP (Bréhat and Wyncke 1988) and several isomorphs as well as KDP (Simon *et al* 1988) have presented temperature dependences of the optical phonons including the highly damped low-frequency mode. In these studies, mode parameters such as frequencies or oscillator strengths have been derived in a wide temperature range by fitting the infrared-reflectivity spectra to a factorized form of the dielectric function. These results were interpreted in terms of the displacive model of the phase transition. It has also been suggested by Tominaga and Urabe (1982) regarding the low-frequency Raman response in KDP that the very-low-frequency ($\lesssim 20$ cm^{-1}) central component, which is also strongly temperature dependent, should be noted. At present, despite many experimental efforts, no conclusive evidence of proton tunnelling or phonon softening in KDP has been obtained.

Recent Raman-scattering experiments by Tominaga *et al* (1983a, b) and neutron-diffraction structural redetermination by Nelmes *et al* (1982) have suggested another viewpoint concerning the transition: the transition is of order–disorder type, in which the distorted tetrahedral PO_4^{3-} units carry the permanent local dipole moment and order at T_c. A heavily damped low-frequency mode observed in the Raman spectra above T_c has been attributed to the librational motion of the PO_4 tetrahedra, which must couple to the polarization fluctuation (Tominaga *et al* 1983a). Recently Sugimoto and Ikeda (1991) proposed a model of the phase transition based on the order–disorder picture, which qualitatively accounts for the isotope effect without assuming proton tunnelling.

Several neutron-scattering studies on KDP have recently been reported. Both incoherent and Compton scattering of neutrons by the protons in KDP have been reported by Ikeda *et al* (1992). The local modes of protons in KDP have been studied by Shibata and Ikeda (1992). They found a relatively low-energy inelastic peak (excitation energy, 28 meV) at low temperatures in addition to the high-energy vibrational modes. Since this mode has an energy that is lower than that of the usual proton local modes ($\hbar\omega > 100$ meV), which seems to disappear above T_c, much attention has been attracted. We report on a further investigation of this excitation in partially deuterized DKDP as well as in KDP. The temperature dependence of the scattering intensity and the difference between KDP and DKDP are discussed. Based on the temperature variation of the incoherent elastic scattering, the temperature dependence of the thermal parameter for the proton has been deduced. The mode polarization of the protons is discussed based on the angle dependence of the scattering intensity. Finally, using single-crystal DKDP (98% D), coherent-scattering measurements were carried out in order to investigate this excitation from the viewpoint of lattice dynamical aspects.

2. Incoherent-scattering measurements

All the neutron-scattering experiments were performed at the spallation pulsed-neutron source (KENS) at the National Laboratory for High-Energy Physics (KEK) located in Tsukuba, Japan. As has already been demonstrated (Ikeda and Watanabe 1987), recent developments in neutron spectroscopy, which utilize the spallation pulsed-neutron and TOF (time-of-flight) method enable higher-energy excitation measurements with better energy resolutions than in earlier experiments. Here, we discuss mainly this unassigned 28 meV

mode; other detailed features, such as the higher-energy proton local modes or molecular vibrational levels, will be reported elsewhere.

For neutron incoherent inelastic scattering from protons, the differential cross section for the neutron energy loss is expressed as (Lovesey 1984)

$$\left(\frac{d^2\sigma}{d\Omega\, d\omega}\right)_i^+ = \frac{k_f \sigma_i}{k_0 8\pi} \sum_{\lambda,q} [n(\omega_q^\lambda) + 1] \exp[-2W_\lambda(Q)] |Q \cdot c_q^\lambda|^2 \frac{\delta(\omega - \omega_q^\lambda)}{\omega_q^\lambda} \tag{1}$$

where c_q^λ is the displacement vector for the mode labelled λ, and should be proportional to $(M_{\text{proton mass}})^{-1/2}$. We assume here harmonic vibrations for the proton motion. The orientational average will be considered in order to analyse scattering from a polycrystalline sample.

The temperature variation of the inelastic-scattering spectrum of KDP was measured using the crystal-analyser inelastic spectrometer CAT at KENS. In the CAT spectrometer the energy of the scattered neutrons is fixed at 3.9 meV by a pyrolytic-graphite crystal analyser in the time-focused configuration, and a cooled Be filter is used to eliminate any higher-order contamination from the analyser. This type of spectrometer is especially effective for observing incoherent scattering. A powdered specimen was packed with He exchange gas into a sample cell having a size of $70 \times 70 \times 2$ mm^3, and was cooled by a closed-cycle refrigerator. Measurements were carried out at temperatures of 25, 80, 115, 128 and 225 K. Some care was needed in order to obtain a uniform temperature distribution over the large sample cell. The resultant temperature dependence of the inelastic spectrum is shown in figure 1. The same experiments as for KDP were carried out for partially deuterized DKDP in order to determine the relation between the transition temperature and the excitation energy of this mode. The deuterization ratio of the prepared specimen was estimated to be 90% from T_c (= 210 K), which was determined using a differential scanning calorimeter. The results are given in figure 2. The general feature is similar to that observed for KDP, showing a drastic change in its behaviour at T_c. The peak position, energy width and integrated intensity are plotted in figure 3, and show the temperature variation of the peak profile. Since the intensity inevitably depends upon the estimation of the background, it is difficult to accurately derive the intensity change at T_c. The temperature dependence of the Debye–Waller factor has not been separated from the plotted intensity variation. It is safe, however, to conclude that the peak does not disappear, but significantly broadens at T_c when the temperature is raised. For DKDP (90% D) no meaningful background subtraction is possible for the spectra above T_c. It should be noted that the peak is slightly shifted (by 2 meV) upon deuteration to the higher-energy side.

If the peak comprises a single normal mode, it is possible to determine the eigenvector of the mode according to expression (1), even based on incoherent scattering. Although the angle dependence of the scattered intensity of the 28 meV mode had already been reported by Shibata and Ikeda, a measurement with a better Q (or angular) resolution was needed. The MAX crystal-analyser inelastic spectrometer at KENS was used for this purpose. MAX (designed for studies of collective excitations in single crystals) has 15 analyser–detector systems in which the energies E_f of the scattered neutrons are arbitrarily selectable (Tajima *et al* 1982, Todate *et al* 1990). In the measurement, the E_f of each detector was selected so that the magnitude of the scattering vector Q became 5 Å^{-1} for an energy transfer of 28 meV. The typical Q resolution $\Delta Q/Q$ is 3%, and the energy widths $\Delta\hbar\omega$ are smaller than 3.5 meV at $\hbar\omega = 28$ meV. By rotating the sample crystal in the *ac* plane, TOF spectra were collected at 18 K. The normalized integrated intensities of the peak are plotted in figure 4 as a function of the angle between the a axis and Q.The intensity difference due to

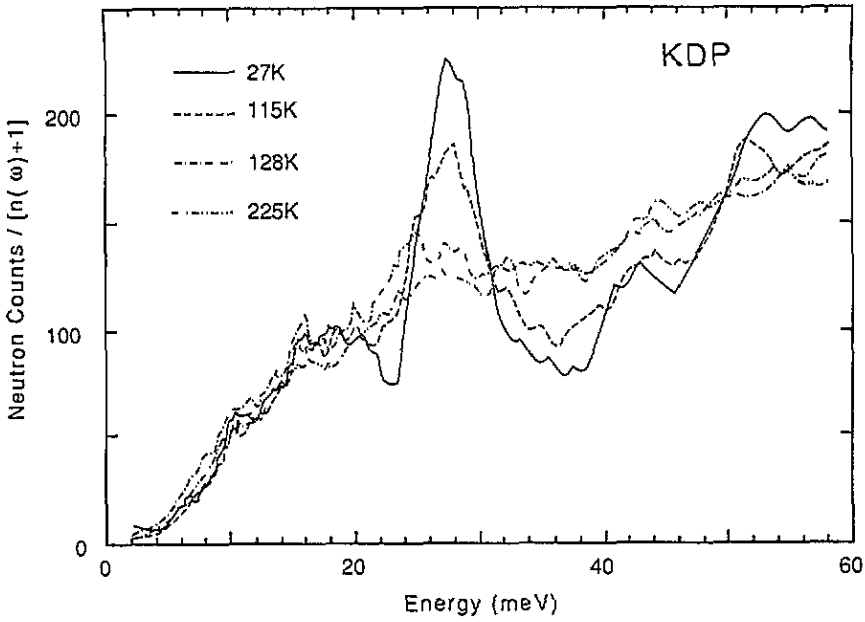

Figure 1. Temperature dependence of the incoherent inelastic scattering from KDP. The spectra were normalized using the Bose factor.

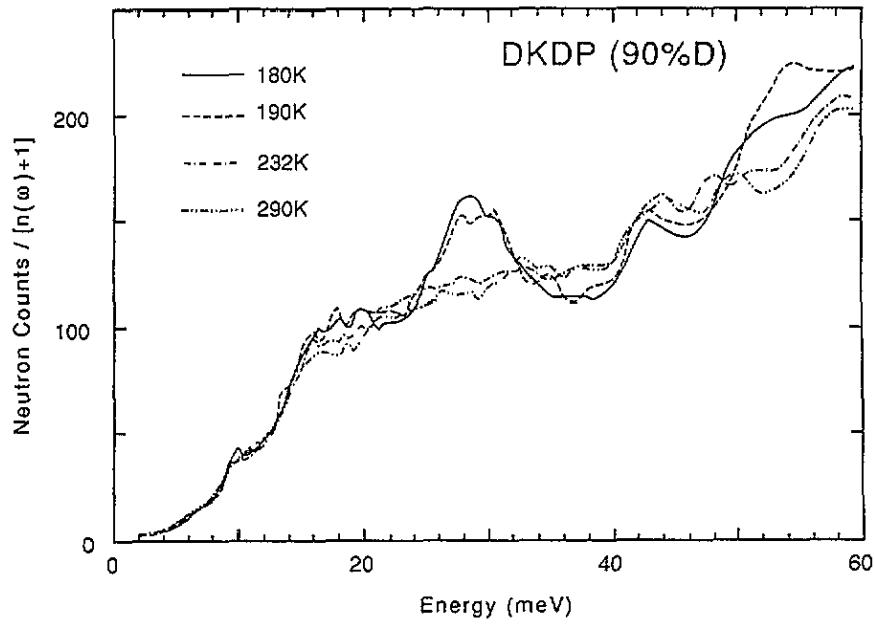

Figure 2. The same plot as in figure 1, but for DKDP (90% D). Note that the peak at 29 meV seems to be due to incoherent scattering from the residual 10% protons in the sample.

the anisotropic Debye–Waller factor (Bacon and Pease 1955, Nelmes *et al* 1982) is not large at low temperatures, and was therefore neglected. The maximum intensity was obtained

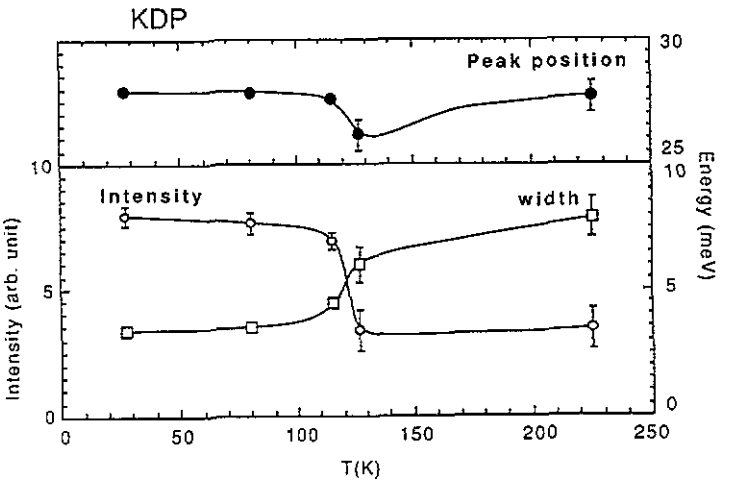

Figure 3. Temperature dependences of the peak position, the energy width and the integrated intensity for the 28 meV peak in KDP. The curves are guides to the eye.

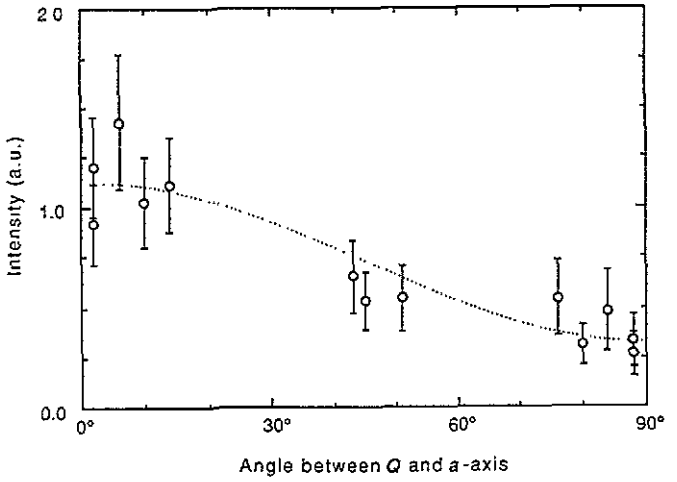

Figure 4. Plot of the integrated intensity of the 28 meV peak as a function of the angle between the a axis and the scattering vector $\boldsymbol{Q}$. The curve indicates the expression $c_{xy}^2 \cos^2\theta + c_z^2 \sin^2\theta$, where c_{xy} and c_z are the xy and z components respectively of the mean amplitude.

for the case when $\boldsymbol{Q} \parallel \boldsymbol{a}$ and was minimum for $\boldsymbol{Q} \parallel \boldsymbol{c}$. As far as the proton motion is concerned, as a result, the predominant character of the mode is that of stretching with respect to the hydrogen bond, as has already been reported. It should be noted, however, that the intensity in the $\boldsymbol{Q} \perp \boldsymbol{a}$ configuration is much larger than that resulting from the finite instrumental resolution effect in the case of a vanishing inelastic structure factor, i.e. in the case where the mode eigenvector is exactly perpendicular to $\boldsymbol{Q}$.

The incoherent elastic intensity is directly related to the Debye–Waller factor for a proton, i.e.

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_i^{\mathrm{el}} = (N\sigma_i/4\pi)\exp[-2W(\boldsymbol{Q})]. \tag{2}$$

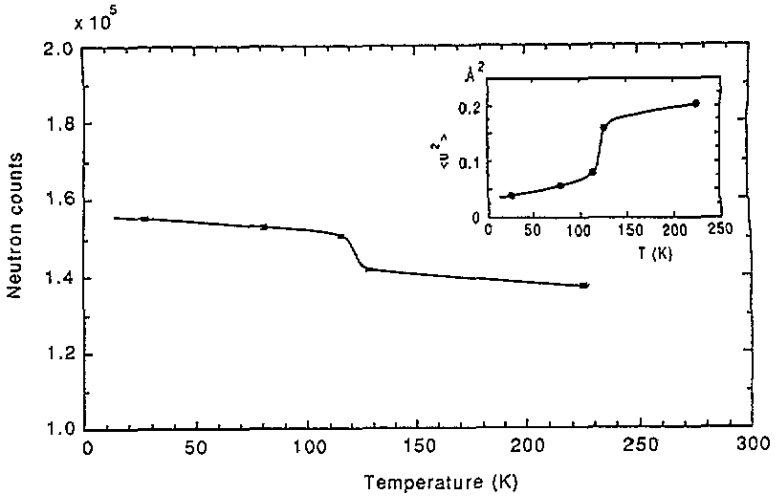

Figure 5. Temperature dependence of the integrated incoherent elastic intensity for KDP. Note that the scattering intensity is almost entirely due to the proton. The inset is the mean square displacement for the proton, which is normalized at $T = 80$ K using a value estimated by Bacon and Pease (1955) at 77 K.

Therefore, the temperature variation of the mean square displacement can be accurately determined. Figure 5 demonstrates the determination of the Debye–Waller factor for the protons in KDP measured by the CAT spectrometer. The inset is the mean square displacement for a proton which is normalized at $T = 80$ K by using a value estimated by Bacon and Pease (1955) at 77 K. The discontinuity at T_c is clearly attributable to the proton localization below T_c.

3. Coherent-scattering measurements

Although the observed proton motion in KDP and DKDP is obviously related to the phase transition, the mode has not yet been assigned. The +7% shift of the energy of the mode on 90% deuteration suggests that this mode does not correspond to the 'collective' proton (deuteron) tunnelling, which is assumed to exist in the proton-coupled soft-optic-phonon model, but simply shows that the local environment for the 10% proton in DKDP (90% D) does not significantly vary due to deuteration. It seems to be worth while to observe the coherent response of the lattice and to investigate the relation between the 28 meV mode motion and the formation, or fluctuation, of the dipole moments, since in this energy region the proton motion cannot be independent of the motion of the surrounding atoms (Reid 1959). From this point of view, we performed coherent-inelastic-scattering measurements on a single crystal of DKDP. The TOF scan was made along the tetragonal a^* axis within the ac plane using the MAX inelastic spectrometer described before; the excitation spectrum around the (303) and (503) reciprocal lattice points was obtained. Note that intense temperature-dependent quasi-elastic scattering was observed at these points in DKDP (Skalyo *et al* 1970, Paul *et al* 1970). The coherent scattering cross section for one-phonon creation can be written as

$$(\mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}\omega)_c^+ \propto (k_f/k_0)[n(\omega)+1]|F(\boldsymbol{Q})|^2\omega\Gamma/[(\omega_0^2-\omega^2)^2+(\omega\Gamma)^2] \qquad (3)$$

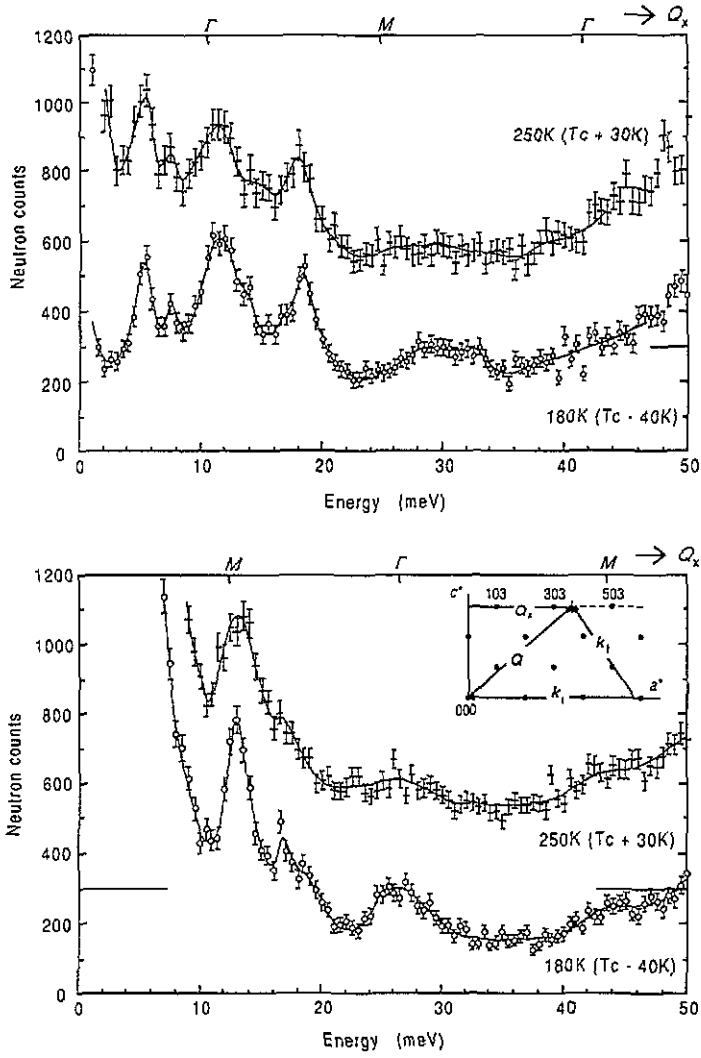

Figure 6. Examples of the coherent-scattering spectra measured on single-crystal DKDP both above and below T_c. The inset is a scattering diagram for the TOF measurement along the a^* direction through the (303) and (503) reciprocal lattice points. The upper set of spectra corresponds to a scan that passes through the zone boundary with an energy transfer of $\hbar\omega = 30$ meV, while the lower corresponds to the zone centre at the same energy transfer.

where the dynamical structure factor $F(\boldsymbol{Q})$ is given by

$$F(\boldsymbol{Q}) \propto \sum_j b_j(\boldsymbol{Q}\cdot\mathbf{c}_q^j)\exp[-W_j(\boldsymbol{Q})]\exp(\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{r}_j). \tag{4}$$

The degree of deuteration of the present single crystal ($2 \times 2 \times 4$ cm^3) was 98%, and the measurements were carried out at temperatures of 180 K ($T_c - 40$ K) and 250 K ($T_c + 30$ K). The results are given in figures 6 and 7. The upper set of spectra in figure 6 corresponds to the TOF scan which passes through the zone boundary with an energy transfer of $\hbar\omega = 30$ meV, while the lower set corresponds to the zone centre at the same energy

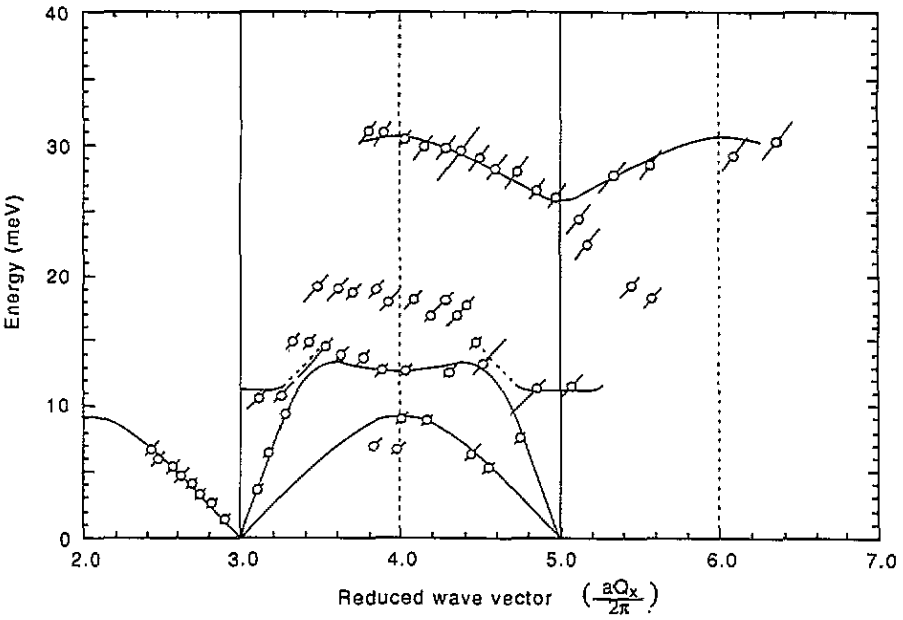

Figure 7. Phonon peaks observed by the TOF scan along the [100] direction at $T = 180$ K. The curves are guides for the eye. The slope of the acoustic branches agrees with a measurement made by Skalyo *et al* (1970).

transfer. Note that the scans are not at constant Q nor at constant E, due to the TOF method. The observed peak positions including the acoustic phonon branches are plotted in figure 7. It is clear that the mode located at about 28 meV has some energy dispersion, and broadens significantly above T_c. This result is, of course, consistent with the incoherent-scattering measurements described before, which show a finite energy width of about 2.5 meV full width at half maximum (FWHM) as well as some structure of the peak, since the incoherent-scattering intensity corresponds to the density of states of the mode. The clarity of the incoherent peak corresponds to a localized character of the mode, thus reflecting the sharp density of states. The collective nature of the excitation indicates that there is a substantial interaction between atoms via hydrogen bonds.

4. Results and discussion

The motion of the protons associated with the 28 meV mode is not a simple two-site excursion along the hydrogen bond. The ratio of the mean z amplitude to the xy component can be estimated from figure 4 to be as large as 54%. A large z component for the proton motion has also been observed in the ferroelectric fluctuation of DKDP, measured by neutron quasi-elastic scattering (Skalyo *et al* 1970). It now seems more plausible to discuss this mode as being a complicated optical mode motion of the atoms, rather than a purely local (single-site) proton mode in the asymmetric double-well potential. It is therefore desirable to extend the coherent-scattering measurement throughout a wider reciprocal space in order to determine the mode-displacement vector from the Q dependence of the dynamical structure factor (4).

It would also be valuable to compare the neutron-scattering spectrum with that obtained by optical measurements. This 28 meV mode may have a close relation to the external (lattice) mode found at about 200 cm^{-1} in the infrared-reflectivity experiments (Wyncke and Bréhat 1986, Bréhat and Wyncke 1988, Simon *et al* 1988). Although the frequency shift measured in our experiments is not large compared with their results, this infrared-active lattice mode also exhibits a remarkable temperature dependence. A comparison between the internal modes obtained from the Raman and neutron-scattering spectra has been made by Mizoguchi *et al* (1993). Here, we note another Raman-scattering experiment (Laulicht 1978) in which the widths of certain A_1 lines in KDP (the 346 and 525 cm^{-1} lines, which we consider to be the internal modes of PO_4) exhibit a temperature dependence similar to that of the 28 meV mode shown in figure 3. On the basis of perturbation theory, which was successfully applied to ammonium halides (Matsushita 1976), qualitative explanations have been given in terms of the pseudo-spin-phonon interaction. The present neutron-scattering results also suggest a contribution of the order–disorder character and the existence of an Ising-spin-like mode, i.e., correlated flipping of atomic groups (Paul *et al* 1970, Nelmes *et al* 1982). The observed mode may be an optic mode that strongly couples to the Ising-spin variable. Since, in this case, the degree of freedom that carries the Ising-spin variable is the translational motion of the ions, the relaxation time of the spins can be as fast as that of the usual phonon frequencies. The dipole moments are considered to be carried by distorted PO_4 tetrahedra (Blinc and Zeks 1982, Tominaga *et al* 1983b), and flipping of the moment is realized by a slight displacement of the ions. Considering these situations, we could further speculate that at low temperatures the dynamics of this pseudo-Ising spin may have a propagating character with the off-diagonal elements in the relevant spin-Hamiltonian description, rather than the stochastic Ising spins in a deep double-well potential, and that this 'pseudo-spin-wave' may be considered as behaving similarly to the observed 28 meV optic mode. We emphasize the importance of the lattice-dynamical description on the formation of the dipole moments and interactions between them in the KDP-type ferroelectrics.

Finally, we point out the temperature independence of the mode frequency. Proton modes, such as the ν(O–H) proton stretching and this 28 meV mode, are more or less dependent on the surrounding atomic displacements. However, from experimental observation, the ν(O–H) mode, the energy of which is 160 meV, does not change in energy over the temperature range from 20 to 300 K, though its line width broadens (Shibala and Ikeda 1992). This temperature independence of the frequency is incompatible with the suggested displacive motion, or the centre-of-mass mode motion in phase with the optical mode motion of the P atom (Nelmes *et al* 1985), which contributes to the formation of the dipole moments. This temperature independence of the mode frequencies seems to be consistent with the unchanged internal-mode frequencies of PO_4 (Tominaga *et al* 1983b).

5. Summary

The relatively low-frequency vibration of the protons in KDP found in neutron incoherent inelastic scattering involves a substantial z component of the proton amplitude. Partial deuterization does not result in any significant changes in the proton motion. It has been revealed from coherent-scattering measurements that the relevant excitation in DKDP has a collective (propagating) nature. It seems to be reasonable to discuss this mode as being an optical-mode motion of the atoms, rather than a purely proton local mode in an asymmetric double-well potential. An abrupt broadening of the inelastic peak at T_c

upon heating has been observed for all of the samples: KDP, DKDP (90% D) and DKDP (98% D). The results suggest that the mode strongly couples to the fluctuation of the dipole moments; a qualitative explanation seems to be given by introducing the Ising-spin variable based on the order–disorder model. However, no relevant microscopic description for the fluctuation has yet been given explicitly. We emphasize that it would be valuable to extend the investigation of the coherent response from single-crystal DKDP by means of neutron scattering. The difference between KDP and DKDP is another important subject to be considered. A comparison of the lattice dynamics with other order–disorder-type materials, such as NH_4Br (Yamada *et al* 1974) or $NaNO_2$ (Sakurai *et al* 1970) would also be valuable.

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