The pressure dependence of tunnelling of coupled pairs of methyl groups in lithium acetate dihydrate

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Abstract. The pressure dependence of tunnelling of coupled pairs of methyl groups in lithium acetate dihydrate has been investigated using the neutron scattering spectrometer IRIS. Methyl tunnelling spectra, recorded at a temperature of 5 K and pressures up to 9.5 kbar, reveal structure which has been attributed to coupling. The data, which extend an earlier investigation by Heidemann et al, have been fitted to a time-independent Hamiltonian, and the fit parameters include the potential barriers of the individual methyl groups and the coupling potential between them. The magnitudes of both parameters increase with increasing pressure and their pressure dependence has been analyzed to provide information on the inter-molecular forces.

1. Introduction

The pressure dependence of methyl tunnelling in lithium dihydrate at 5 K has been investigated using the IRIS neutron scattering spectrometer. The scientific interest in this material arises because it is the best example currently available of coupled pairs of molecular rotors. The methyl groups in the crystal are grouped together in pairs with their planes of rotation separated by 2.5 Å along their common threefold axes [1].

A neutron scattering study by Clough et al [2] of this material on IN5 revealed structure in the tunnelling spectrum which was attributed to coupling. The data were successfully fitted to a model in which a coupling term representing the potential energy of one rotor against its partner was added to the conventional time-independent Hamiltonian. In a further study Heidemann et al [3] observed an increase in both the single-particle potential and the coupling potential with increasing hydrostatic pressure on the material. In the present investigation we have extended the range of applied pressure and improved upon the resolution and statistics of the neutron scattering spectra. The aims of this experiment were to apply pressure to the crystal in order that the tunnelling spectra could be studied and interpreted as changes were made to both the single-particle and coupling potentials. The experiment was performed as a function of pressure up to 9.5 kbar on the IRIS neutron scattering spectrometer at the pulsed neutron source ISIS, Rutherford–Appleton Laboratory (RAL).

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2. Experimental details and results

The IRIS spectrometer is an inverted-geometry time-of-flight spectrometer designed for quasi-elastic and low-energy inelastic spectroscopy [4]. It employs a large pyrolytic graphite crystal analyser in near-back-scattering geometry with 135 separate detector angles. This gives high resolution (FWHM = 15 μeV) over a wide energy transfer range.
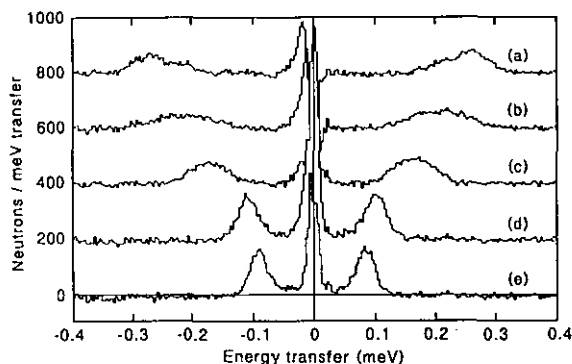

Figure 1. The IRIS spectra of lithium acetate dihydrate recorded at five different pressures and a temperature of 5 K. (*a*) 0.001 kbar, (*b*) 1.2 kbar, (*c*) 4.6 kbar, (*d*) 8.0 kbar and (*e*) 9.5 kbar.

The powdered sample (0.3 cm^3) was mounted inside a clamped pressure cell designed and provided by RAL [5]. The construction material of this cell was steel, aluminium and alumina; only the latter two materials were in the neutron beam. The scattered neutrons from the sample were viewed through approximately 2 cm of aluminium and 2 cm of alumina. Because of the long wavelength of the incident neutron beam no Bragg reflections were excited in the cell material rendering it almost transparent and reducing background effects. The sample temperature was set to 5 K and controlled to an accuracy of 0.2 K for the duration of the experiment. The pressure was applied to the sample at room temperature and the actual pressure of the sample following cooling was determined from a calibration. Each neutron scattering spectrum was recorded for a period of 14 to 16 hours with the ISIS neutron source running at 90 μA. The IRIS data, recorded at five different pressures, are shown in figure 1. In order to achieve good statistics the data from all efficient detectors were added together and a suitable background subtraction was also made to eliminate the scattering from the empty pressure cell. In figure 1 the data recorded at ambient pressure reveal the components in the tunnel spectrum first observed by Clough *et al* [2] on IN5. With increasing applied pressure the average tunnel splitting decreases with the components become narrower and merge together. The intrinsic linewidths, particularly at lower pressures, are broader than the resolution of the spectrometer.

3. Theory and data analysis

In order to connect the measured parameters in the experimental spectra with molecular properties attributable to the tunnelling dynamics of the methyl groups we have made model calculations by solving the time-independent eigenvalue equation using the following Hamiltonian

$$\mathcal{H} = -(\hbar^2/2I)\left(\partial^2/\partial\phi^2 + \partial^2/\partial\theta^2\right) + \left(V_3^{(1)}/2\right)(1 - \cos 3\phi) + \left(V_3^{(2)}/2\right)(1 - \cos 3\theta)$$
$$+ (W/2)(1 - \cos 3(\phi - \theta)). \tag{1}$$

Here $I = 5.31 \times 10^{-47}$ kg m^2 is the moment of inertia of a single methyl group, θ and ϕ are the rotational coordinates of the two methyl groups labelled (1) and (2). $V_3^{(1)}$ and $V_3^{(2)}$ are the threefold single-particle potentials experienced by each methyl group and W is the coupling potential between the two. In order that the physically realistic situation is realized whereby the two methyl groups adopt a staggered configuration with respect to each other we must have $V_3^{(2)} = -V_3^{(1)} = V_3$ [6]. The sign conventions are then compatible and the Hamiltonian is equivalent to those employed in [3] and [6]. Using a basis set $\psi = (1/2\pi) \exp(im\theta) \exp(in\phi)$, consisting of products of free rotor eigenfunctions, the eigenvalues of equation (1) have been calculated by diagonalization of the Hamiltonian matrix. The frequencies ω_0 and $\Delta\omega$ which define the tunnelling spectrum (these are defined below) have been deduced from the calculated eigenvalues and plotted on the contour plots of figure 2 as a function of V_3 and W. The numerical techniques employed to generate figures 2(a) and (b) were identical to those used by Clough *et al* [2], where for each symmetry species a 49×49 matrix was employed. (For the AA species the quantum numbers were confined to the range $-9 \leqslant n, m \geqslant +9$.) The truncation of the matrices in this way leads to no significant error within experimental accuracy in the ground state tunnelling spectrum for the ranges of V_3 and W employed.
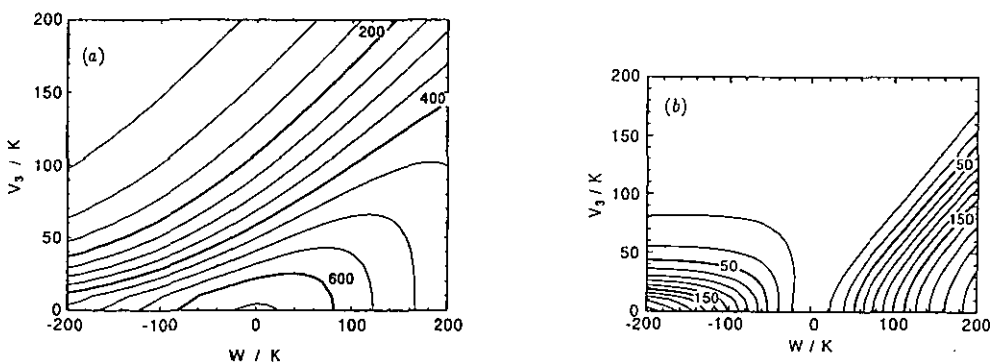

Figure 2. Contour plots of the parameters (*a*) ω_0, and (*b*) $\Delta\omega$, as a function of barrier potentials V_3 and W. These define the tunnelling spectrum of coupled methyl groups in lithium acetate dihydrate. The major contours are identified in μeV units.

For lithium acetate dihydrate, and according to current theories for coupled pairs of methyl groups [2, 6] three lines occur in the tunnelling spectrum with an intensity ratio 1:1:2 with the most intense line occurring at the highest frequency ω_0. Accordingly the IRIS data were fitted to the sum of three Gaussians centred at the frequencies ω_0, ω_1, and ω_2. An example of the fit to a neutron energy gain spectrum is shown in figure 3 where the pressure applied to the sample was 9.5 kbar. In the fitting procedure the intensity ratios were fixed and the linewidths of the individual components were tied together. The fitted, experimental values of ω_0, ω_1, ω_2 and the linewidth are presented in the table. It should be noted that the linewidths quoted include a contribution from the resolution function of the spectrometer. The aim was then to deduce the values of V_3 and W which are consistent with the measured tunnelling frequencies. In the preliminary analysis it was expedient to minimize the number of parameters. Following Heidemann *et al* [3] we used the approximation $\Delta\omega = (\Delta\omega_1 + \Delta\omega_2)/2$ where $\Delta\omega_1 = \omega_0 - \omega_1$
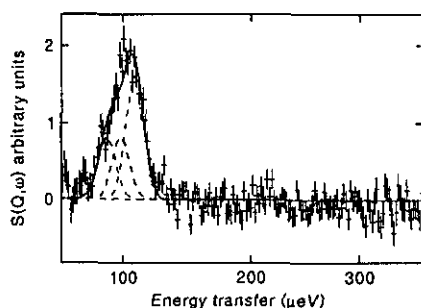
Figure 3. One of the tunnelling peaks recorded at 5 K and 9.5 kbar pressure. This illustrates the fit to three Gaussians as described in the text.

and $\Delta\omega_2 = \omega_1 - \omega_2$. The pressure dependence of ω_0 and $\Delta\omega$ is plotted in figure 4. By overlaying contour plots of $\omega_0(V_3, W)$ and $\Delta\omega(V_3, W)$ (figures 2(a) and (b)) it was possible to deduce the unique values of V_3 and W which are consistent with the experimental data. These are presented in the table and their magnitudes are plotted in figure 5. The coupling parameter W is negative in agreement with Heidemann *et al* [3]. This is consistent with the two methyl groups adopting a staggered configuration as discussed by Häusler and Hüller [6]. Theoretical values of ω_0, ω_1 and ω_2 are also presented in the table and in order to minimize truncation errors these were refined by diagonalization of 121×121 matrices.

Table 1. The pressure-dependence of the measured and calculated tunnelling frequencies in lithium acetate dihydrate and the corresponding single-particle (V_3) and coupling (W) potentials.

Pressure (kbar)	Measured (μeV)					Calculated (μeV)			Potentials (K)	
	ω_0	ω_1	ω_2	$\Delta\omega$	Linewidth FWHM	ω_0	ω_1	ω_2	V_3	W
0.001	266			37.5	75	265	228	191	46.4	−106
1.2	240	190	170	35	70	238	203	169	49	−114
4.6	186	154	133	26	48	186	158	134	57	−126
8.0	110	94	79	15.5	25	111	94	80	70	−161
9.5	91	78	65	13	20	91	77	65	75	−176

4. Discussion

In figure 4 it may be observed that both measured parameters ω_0 and $\Delta\omega$ decrease approximately linearly with increasing pressure. This observation is explained in figure 5 by an increase in the magnitudes of the single-particle potential V_3 and the coupling parameter W, these in turn reflect the increased inter-atomic repulsion as the applied pressure is increased. Qualitatively similar observations were made in the pressure range up to 4 kbar by Heidemann *et al* [3] although their data displayed a slightly more
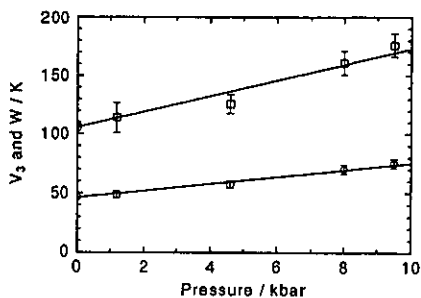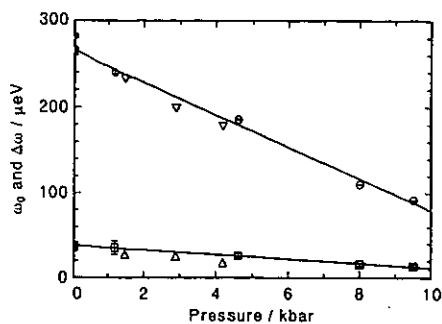
Figure 4. The parameters ω_0 (O) and $\Delta\omega$ ($\square$) as a function of pressure. The lines are guides to the eye. The data of Heidemann *et al* [3] are shown by triangles.

Figure 5. The magnitudes of the barrier parameters $|V_3|$ (O) and $|W|$ ($\square$) as functions of pressure. The straight lines are the fits as described in section 4.

rapid decrease in ω_0 and $\Delta\omega$ with increasing pressure. Their results are included for comparison in figure 4.

The signs of V_3 and W reflect the phase of the potentials, in discussing the pressure dependence of these parameters it will be sufficient to consider the magnitudes $|V_3|$ and $|W|$ of the single-particle and coupling potentials respectively. As pressure is applied to the sample then the increase in $|V_3|$ and $|W|$ reflect the increase in the pairwise inter-atomic potentials between the hydrogen atoms of the methyl group and the atoms of neighbouring molecules. A common phenomenological expression for these potentials is the Lennard-Jones potential where the repulsive component has the mathematical form

$$V_{\text{rep}}(r) = K/r^n. \tag{2}$$

Here K is a constant, r is the inter-atomic distance and, commonly, the exponent n has the value 12. Following the procedure adopted by Clough *et al* [7] and McDonald *et al* [8, 9] we have analysed the pressure dependence of V_3 and W to provide the information on the inter-atomic potentials. Inspection of figure 5 shows that the barrier components V_3 and W both have a linear dependence on pressure, P:

$$V_3(P) = V_3(1 + \alpha_V P) \tag{3}$$

$$W(P) = W(0)(1 + \alpha_W P). \tag{4}$$

Similar observations have been made in previous investigations [7–9] of methyl tunnelling with pressure. The data in figure 5 have been fitted to the above expressions with the following results: $W(0) = -105.5 \pm 2$ K; $\alpha_V = 0.064 \pm 0.005$ kbar^{-1}; $V_3(0) = 46.2 \pm 1$ K; $\alpha_W = 0.063 \pm 0.002$ kbar^{-1}. Differentiation of equations (3) and (4) gives the following expression for α_V

$$\alpha_V = (1/V_3(0))(\partial V/\partial r)\partial r/\partial P \tag{5}$$

and a similar one for α_W. If we assume the repulsive potential given by equation (2) then,

$$\alpha_V = [-(n+1)/r]\partial r/\partial P. \tag{6}$$

Given the bulk compressibility $\kappa = (-3/r)\partial r/\partial P$ we obtain by substitution in equation (6),

$$\alpha_V = [(n_V + 1)/3]\kappa \tag{7}$$

and similarly

$$\alpha_W = [(n_W + 1)/3]\,\kappa. \tag{8}$$

Typical values for κ in molecular solids [10] are of order 0.01 kbar^{-1} so we may deduce the values of the exponents n_V and n_W from the two sets of data. Assuming $\kappa = 0.01$ kbar^{-1}, and neglecting any systematic errors associated with this approximation, the results are $n_V = 17.9\pm0.5$ and $n_W = 18\pm2$ and these are clearly identical within experimental error. This is a very satisfactory result as it confirms that the fundamental physical origins of the inter-atomic potentials which compose V_3 and W are similar. The absolute values of the exponents n are however somewhat larger than the value $n = 12$ commonly assumed for a Lennard-Jones potential. This may reflect the estimate employed for κ, if we were to assume $\kappa = 0.014$ kbar^{-1} (which is within the range of commonly accepted values) then this discrepancy would be alleviated. At present no independent measurement of κ exists for lithium acetate dihydrate.

5. Conclusions

Pressure dependence measurements of methyl tunnelling in lithium acetate dihydrate are consistent with theories which include mechanical coupling between the rotors in addition to the single-particle potentials. With increasing pressure both $|V_3|$ and $|W|$ potentials increase linearly. The relative quantities $\Delta V_3/V_3$ and $\Delta W/W$ increase in the same proportion indicating that the origins of V_3 and W are similar and may be attributed to repulsive components of the inter-atomic forces. The use of pressure-dependence studies of methyl tunnelling as a probe of inter-atomic and inter-molecular potentials has been shown to be one of great promise, particularly when coupling is present. However, in order to eliminate systematic errors associated with (a) estimation of the bulk compressibility, and (b) assumptions of linear scaling of interatomic distances, it would be necessary to complete a diffraction study of the crystal structure as a function of pressure.

Acknowledgments

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