Deuteron Magnetic Resonance Studies

Part 6.—Lithium Deuteroxide Deuterate

By John O. Clifford,† John A. S. Smith* and Francis P. Temme‡

Chemistry Department,
Queen Elizabeth College, Campden Hill Road, London W8 7AH

A deuteron magnetic resonance study of single crystals of $LiOD \cdot D_2O$ at 82 K has shown that the crystal is ordered and that the deuteron quadrupole coupling constants and asymmetry parameters for the OD^- ion and D_2O molecule are

$$OD^- (e^2qQ/h) = 271.7 \text{ kHz}, \eta = 0.04_3$$
$$D_2O(e^2qQ/h) = 173.0 \pm 0.9 \text{ kHz}, \eta = 0.16_9 \pm 0.005.$$

The OD^- ion points along the c-axis of the crystal and the plane of the water molecule is perpendicular to the same direction, giving rise to strong but markedly non-linear $O_h \ldots O_w \ldots O_h$ hydrogen bonds between the two species. The angle between the two maximum principal components of the quadrupole coupling tensor in one D_2O molecule is $107°15'$, larger than that observed in D_2O vapour $(101°59')$, the difference being attributed largely to an expansion of the $\widehat{DOD}$ angle by $5 \pm 2°$ when the water molecule enters the lattice of $LiOD \cdot D_2O$. The temperature dependence of the quadrupole coupling constant of the OD^- ion is governed by its torsional modes; in the neutron inelastic scattering spectra these appear near 642 cm^{-1} in $LiOH \cdot H_2O$ and 468 cm^{-1} in $LiOD \cdot D_2O$.

Only one measurement of the deuteron quadrupole coupling constant [1] in the OD^- ion has been reported in the literature, that in $LiOD$.[2] We present here a deuteron magnetic resonance study of $LiOD \cdot D_2O$, in which the deuteron quadrupole coupling tensors for both OD^- and D_2O are deduced and compared with the crystal structure. Neutron inelastic scattering measurements on the protonated and deuterated salts are also performed in order to clarify the origin of the temperature dependence of the quadrupole tensor.

EXPERIMENTAL

Lithium hydroxide monohydrate is monoclinic, space group $C2/m$ (C_{2h}^3), with $a = 7.37$, $b = 8.26$, $c = 3.19$ Å, $\beta = 110°18'$ and $Z = 4$.[3,4] The same symmetry is assumed to be valid for the deuterated salt, which is consistent with the deuteron resonance rotation patterns. Crystals of the deuterated form were grown in a small desiccator thermostatted at $32.0 \pm 0.1°C$ by the method of Sampson and Di Piettro.[5] The solution was prepared by dissolving Li_2O in 99.8 % D_2O and the salt allowed to crystallize out to obtain suitable seeds; with one of these, a crystal $10 \times 10 \times 4$ mm grew over a period of five weeks. The crystal was mounted in a polystyrene sample holder connected at the top via the coaxial line to a large copper can containing the coolant. The coaxial line ran on to an aluminium plate to which it was accurately perpendicular; the plate itself was set by spirit levels and adjusting screws to be horizontal, so that the rod supporting the sample was accurately vertical.

The crystal was glued with Araldite to the top of a supporting rod whilst the latter was mounted on an X-ray goniometer; as the glue hardened, X-ray back reflection oscillation photographs were taken and the crystal adjusted until the c-axis layer lines were horizontal.

† present address: Leamington College, Leamington Spa.
‡ present address: School of Chemistry, University of Bristol, Bristol BS8 1TS.

We established the azimuth by indexing the reflections using the reciprocal axis construction,[6] finally reducing the oscillation range to 5° and moving the crystal 2° at a time; the orientation of a given crystallographic axis perpendicular to [c] was then compared with the reflection of a Webbsky slit from a mirror attached to the mounting rod. In this way, the orientation of the crystal with respect to the mirror normal was established to an accuracy of less than 1°. The whole assembly was then placed in a Dewar flask and mounted in the magnetic field: the orientation of the mirror normal with respect to the magnetic field was established by a technique already described.[7] The c-axis rotation pattern was then recorded at two temperatures (82 and 273 K) by rotating the crystal on its (calibrated) base. Rotation patterns were also recorded about two other axes, making use of the observation that our crystal had one good face parallel to [c]. The second axis [2] was selected so as to give optimum filling factor and had the edges of the good face horizontal, so that it was perpendicular to [c]. The third axis [3], mutually perpendicular to the other two, was selected as follows. The crystal, mounted about [2] was turned on the goniometer arcs through 90° in such a way that the plane of the mirror became horizontal (checked by means of a vertical light-beam); the second mounting axis, [2], was then horizontal. Knowing the angle between [c] and the normal to the mirror (D), we were then able to rotate the crystal about [2] so as to bring [c] into a horizontal plane. With [c] and [2] both in a horizontal plane, a second sample holder was then brought down vertically onto the crystal and the crystal re-cemented to the upper holder, giving us axis [3]. The azimuth was located from the rotation patterns themselves, since each pattern will show two positions 90° apart when the spectrum will be identical to that found in rotation patterns about the two other axes; for example, [3] will show such identities when H is parallel to [2] and [c], and [2] when H is parallel to [c] and [3], the common spectrum giving us the direction of [c]. These assignments were checked after the experiments by means of X-ray back-reflection photographs and found to be consistent; the method assumes that the space group $C2/m$ is true for the hydrogen atoms, but a recent refinement[8] of the original X-ray work[3,4] supports this contention.

Deuteron magnetic resonance spectra were recorded at 18.3 MHz using a Robinson oscillator[9] and a Varian V-3800 15 inch electro-magnet. The oscillator followed closely the design of Pearson[10] and gave r.f. levels of 1 mV to 250 mV between 200 kHz and 25 MHz; for LiOD $\cdot$ D_2O, we used r.f. levels of 100 mV at 273 K and 80 mV at 82 K into a 7-turn coil, diameter 1 cm, made of 24 s.w.g. copper wire. The oscillator was frequency-modulated at 519 Hz with a depth of modulation of 0.1 mT, the spurious amplitude modulation thereby generated being removed by a differential amplifier. The signal then passed on to a phase-sensitive detector and a Servoscribe recorder; with a recording time constant of 4 s and a field sweep rate of 0.5 mT min^{-1}, we achieved a signal-to-noise ratio of about 6 : 1. The magnet provided a field-sweep linear to $\frac{1}{2}\%$ and a working reproducibility of 0.1 mT at 2.803 T.

For the measurements at 273 K, a small capillary containing liquid D_2O was placed near the crystal within the r.f. coil to provide an extra line at the centre of sweep; by this means, we were able to confirm the absence of second-order effects (which shift the centre of gravity of the spectrum).

Spectra were recorded at 10° intervals about the three axes [c], [2], and [3] at temperatures of 82 and 273 K; the c-axis pattern at 273 K has been published elsewhere.[11]

Neutron inelastic scattering experiments have also been performed on polycrystalline LiOH $\cdot$ H_2O and the completely deuterated salt, both at ambient temperatures; the energy gain spectra were recorded on the 6H time-of-flight spectrometer and the energy loss spectra on the cold beryllium filter version of the PLUTO triple axis-spectrometer, both at A.E.R.E., Harwell. The results were corrected and reduced to the form of a differential scattering cross-section by standard methods and the experimental weighted frequency distribution, $g(\omega)$, was derived for LiOH $\cdot$ H_2O by the method of Egelstaff.[12] The LiOD $\cdot$ D_2O results are restricted to large energy transfers and to $|Q|$ values for which the incoherent approximation for coherent scatterers applies.[13] The energy loss results were obtained with a scattering angle of $2\theta = \pi/2$. The infra-red spectra of a powdered sample were recorded on a Perkin–Elmer 621 spectrometer.

RESULTS AND DISCUSSION

The space group $C2/m$, together with the presence of 4 molecules in the unit cell, predicts three pairs of resonance lines at any general orientation, as observed. The crystals are therefore ordered and the water molecules are not flipping about their two-fold axis. We can distinguish therefore between two water deuterons, labelled 2 and 2', and a deuteroxide deuteron, labelled 1. The rotation patterns were fitted graphically to an equation of the form

$$y = A + B \sin 2\theta + C \cos 2\theta \qquad (1)$$

neglecting second-order effects, and the field gradient tensor was diagonalized by a method of successive approximations.[14] The magnitudes of the principal components of the quadrupole coupling tensor ϕ_{xx}, ϕ_{yy}, ϕ_{zz}, together with their direction cosines with respect to the crystallographic axes a^*, b, and c ([a^*] is perpendicular to [b] and [c]), are shown in tables 1 and 2 for temperatures of 273 and 82 K respectively.

TABLE 1.—QUADRUPOLE COUPLING TENSORS FOR THE D$_2$O DEUTERONS (D2, D2') AND THE OD⁻ DEUTERON (D1) IN LiOD·D$_2$ AT 273 K (ABSOLUTE SIGNS ARE NOT DERIVED)

D1 $\phi_{zz} = -267.9$, $\phi_{yy} = 139.9$, $\phi_{xx} = 128.0$ kHz, $\eta = 0.04_4$
eigenvectors

	ϕ_{zz}	ϕ_{yy}	ϕ_{xx}
[a^*]	0	0	1
[b]	0	1	0
[c]	1	0	0

D2 $\phi_{zz} = -173.8$, $\phi_{yy} = 102.0$, $\phi_{xx} = 71.8$ kHz, $\eta = 0.17_4$
eigenvectors

	ϕ_{zz}	ϕ_{yy}	ϕ_{xx}
[a^*]	−0.8070	0.2871	0.5297
[b]	0.5901	0.4144	0.6847
[c]	−0.0149	0.8634	−0.5036

D2' $\phi_{zz} = -172.1$, $\phi_{yy} = 100.2$, $\phi_{xx} = 71.9$ kHz, $\eta = 0.16_4$
eigenvectors

	ϕ_{zz}	ϕ_{yy}	ϕ_{xx}
[a^*]	0.8033	−0.2844	−0.5263
[b]	0.5961	0.3995	0.6945
[c]	0.0122	−0.8712	0.4901

If the space group $C2/m$ is correct (and there is no present evidence to the contrary) deuterons D2 and D2' should be related by the two-fold axis of the crystal and should have identical quadrupole coupling constants and asymmetry parameters; a comparison of these quantities for D2 and D2' therefore gives an estimate of the experimental errors. We estimate for D$_2$O

$$(e^2qQ/h) = 173.0 \pm 0.9 \text{ kHz}, \qquad \eta = 0.16_9 \pm 0.005$$

at both 273 and 82 K, and for OD⁻

$$(e^2qQ/h) = 271. \text{ kHz}, \qquad \eta = 0.04_3$$

at 82 K and

$$(e^2qQ/h) = 267.9 \text{ kHz}, \qquad \eta = 0.04_4$$

at 273 K (each coupling constant having an error of between 1.0 to 1.5 kHz).

Several conclusions may be drawn concerning the crystal structure of $LiOD \cdot D_2O$.
(a) The D_2O molecules are in ordered positions with the two-fold axis of the crystal coincident with the bisector of the $D\widehat{O}D$ angle.   The reliability of this conclusion may be judged from the [b] direction cosines of ϕ_{zz} in table 1 for D2 and D2′, which are 53°50′ and 53°25′.

(b) Static disorder is ruled out by the number of deuteron resonance lines observed and the symmetry of the rotation patterns, and there is no evidence for free rotation or hindered rotation of large amplitude, particularly in view of the insensitivity of the D_2O deuteron quadrupole coupling constants to change in temperature.

(c) The [c] direction cosines of ϕ_{zz} for D2 and D2′ are 89°9′ and 89°18′, so that the plane containing the two components is very close to perpendicularity with [c].

(d) The O–D vector is very close to parallelism with [c], in agreement with infra-red [15] and X-ray evidence.[8]   The conclusions concerning directions in (c) and (d) are (we estimate) accurate to within at least 1°, but their precise structural significance depends to some extent on the relationship of the deuteron quadrupole coupling tensor to the electronic structure of the water molecule in the crystal, to which we now turn our attention.

TABLE 2.—QUADRUPOLE COUPLING TENSORS FOR THE D_2O DEUTERONS (D2, D2′) AND THE OD^- DEUTERON (D1) IN $LiOD \cdot D_2O$ AT 82 K (ABSOLUTE SIGNS ARE NOT DERIVED)

D1 $\phi_{zz} = -271.7$, $\phi_{yy} = 141.7$, $\phi_{xx} = 130.0$ kHz, $\eta = 0.04_3$
eigenvectors

	ϕ_{zz}	ϕ_{yy}	ϕ_{xx}
[a*]	0	0	1
[b]	0	1	0
[c]	1	0	0

D2, D2′ experimental rotation patterns indistinguishable from those at 273 K.

In the gaseous water molecule, the deuteron quadrupole coupling constant is 307.95 kHz, $\eta = 0.1350$ and the angle θ_D between the two directions of ϕ_{zz} is 101°59′ [16] for a bond angle θ_B of 104°31′, that is ϕ_{zz} deviates from the O—H bond direction by an amount $\alpha = 1°16′ \pm 3′$ towards the other proton.   Most theoretical calculations also predict such a deviation but in the opposite direction (i.e. $\theta_D > \theta_B$); values of α range from 0°58′ to 2°40′ according to the quality of the basis set of wavefunctions [17-22] used and are not markedly affected by allowance for zero point motions.[22]   Experimentally it is clear that there is a significant difference between θ_D in D_2O vapour (101°59′) and that in crystals of $LiOD \cdot D_2O$ (107°15′).   In the free D_2O molecule the value of α has been interpreted [17] in terms of the change in the shielding of one deuteron by the electronic charge near the oxygen atom in the other O—D bond: thus α increases as the O—H bond is stretched or the $H\widehat{O}H$ angle decreased.   These changes, however, are small, and even with the predicted changes [23,24] in the O—H bond length in the strongly hydrogen-bonded $LiOH \cdot H_2O$ would amount to little more than 12 minutes.   The changes in α with respect to variation in the $H\widehat{O}H$ angle are also small, and this angle itself changes by usually less than 10° when the H_2O molecule is incorporated into a hydrate lattice,[25,26] a variation which would alter α by less than 1°.[17]   Theoretical calculations have also been made [27] of the effect on the quadrupole tensor of D_2O when it enters the salt lattices of $NaDC_2O_4 \cdot D_2O$ and $LiDC_2O_4 \cdot D_2O$; the value of α drops to 20′ and 53′ respectively, again small changes, in agreement with experiment for $NaDC_2O_4 \cdot D_2O$.[28]   Concerning the possibility

that q_{zz} is twisted out of the plane of the molecule, this is unlikely to produce a deviation larger in magnitude than α in the free water molecule (1°16'), since the closest atom which could be responsible for such a perturbation is the hydrogen-bonded oxygen of the hydroxide ion, about 1.7 Å away (the H . . . H approach within the H$_2$O molecule is about 1.6 Å).   In K$_2$C$_2$O$_4$ · H$_2$O in which (as in this crystal) the H$_2$O molecule lies on the 2-fold axis of a monoclinic crystal and is twisted out of the plane of the water oxygen and the two hydrogen-bonded oxygen atoms, the proton–proton vector makes an angle ϕ_0 of 46.8 $\pm$ 0.2° with [a], whereas in K$_2$C$_2$O$_4$ · D$_2$O, the direction cosines of the principal components of the deuteron quadrupole coupling tensor show that the plane containing the two maximum components ϕ_{zz} makes an angle of 47.0 $\pm$ 0.2° with [a]; there is therefore no significant twist in this crystal of the ϕ_{zz} plane of the two deuteron tensors away from the plane of the water molecule.[29] In NaDC$_2$O$_4$ · D$_2$O[28] the principal axis ϕ_{zz} of one of the deuteron tensors is twisted out of the D$_2$O plane by less than 1°.   Present evidence therefore supports the conclusion that the increase in θ_D on going from the D$_2$O molecule in the vapour phase to that in LiOD · D$_2$O is most likely to be due to a small increase in the D$_2$O angle of 5 $\pm$ 2°.
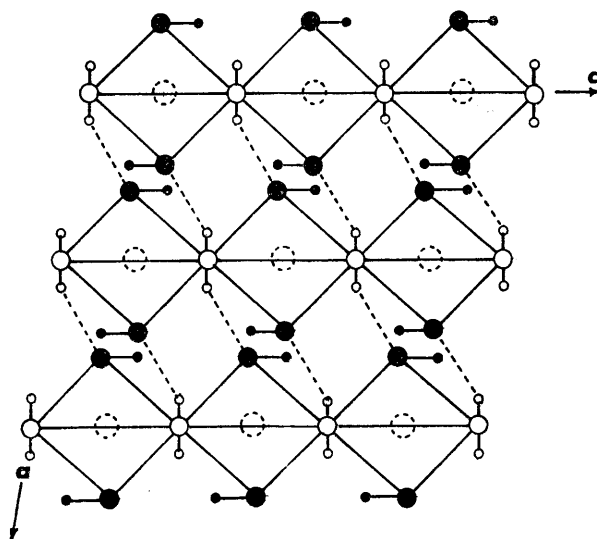

FIG. 1.—Projection of crystal structure of LiOH · H$_2$O down the b-axis with the hydrogen positions (small circles) inferred from the deuteron magnetic resonance results (open circles, H$_2$O atoms; closed circles, OH$^-$ atoms; broken circles, Li$^+$).

The deuteron magnetic resonance data also establish that the hydrogen-bonds in LiOH · H$_2$O are bent.   Fig. 1 shows a projection of its crystal structure down the b-axis with the new hydrogen positions correcting those previously published,[8] assuming that the structure of LiOD · D$_2$O is close to that of LiOH · H$_2$O.

The O$_h$ . . O$_w$ . . O$_h$ angle (O$_h$ = hydroxyl oxygen, O$_w$ = water oxygen) is 100°36' compared to an $\widehat{HOH}$ angle in water vapour of 104°31', and the plane of the same three oxygen atoms makes an angle of 69°42' with [c].   However, the plane containing the two z-direction cosines (table 1) makes an angle of 89°14' $\pm$ 5' with [c], and from previous discussion, we may take this plane to be very nearly coincident with that of the water molecule.   This twist of nearly 20° about [b] is unusually large, and is attributed to the action of the nearest Li$^+$ ions.   These form layers parallel to [c],

and the lithium ions and water oxygens O_w all lie in the bc-plane (fig. 1), the Li—O_w—Li angle being 107°20′, i.e. close to the tetrahedral angle.   If there is a strong interaction between the lone pair electrons on O_w with two adjacent Li^+ ions, the most favourable orientation for the plane of the water molecule would then be that which we infer from the deuteron resonance results.   Such a rotation would be in partial agreement with the infra-red results of Drouard [15] who found the plane of the water molecule to be inclined by about 10° to [$a*$].   This twist of the O_h . . O_w . . O_h plane results in a bending of about 26° in the hydrogen-bond at the deuteron.   It is then of interest to note that the asymmetry parameters of the water deuterons in LiOD · D_2O (0.16$_4$, 0.17$_4$) are among the highest hitherto observed in a hydrate [β-(COOD)$_2$ · 2D_2O having $\eta = 0.16^{30}$].   Furthermore, the directions of ϕ_{yy} with respect to the perpendicular to the plane of the water molecule (derived directly from the [c] direction cosines in table 1) are 30°18′ and 29°24′ (average of 29°51′).   In H_2O vapour, these angles are 0° by symmetry, and in most hydrates lie between 0 and 15°, the largest value hitherto (24°) being found in β-(COOD)$_2$ · 2D_2O.[30]   Chiba has related this distortion in the latter crystal to the non-linearity of the hydrogen-bond, an explanation which is consistent with the LiOD · D_2O results.   The theoretical calculations for $NaDC_2O_4$ · D_2O previously referred to [27] also agree with this generalisation.

TABLE 3.—WAVENUMBERS ($\bar{v}$/cm^{-1}) OF MODES OBSERVED IN THE INFRA-RED AND NEUTRON ENERGY-GAIN AND ENERGY-LOSS SPECTRA OF LiOH · H_2O COMPARED WITH THE RAMAN DATA FOR LiOH · H_2O AND THE NEUTRON ENERGY-GAIN SPECTRUM OF LiOD · D_2O.

| | | LiOH · H_2O | | | LiOD · D_2O |
neutron energy-loss	neutron energy-gain	$g(\omega)$	infra-red	Raman[15]	neutron energy-gain
1100 (sh)	—	—	1140	840 (B_g)	641
1011 ± 23	—	—	975	797 (A_g)	468
953 ± 21	—	—	842	518 (A_g)	379
860 (sh)	—	—	720	396 (B_g)	
799 ± 16	794 (sh)	—	672	365 (B_g)	
642 ± 11	639	640	629	246 (B_g)	
527 ± 8	—	—	455	210 (A_g)	
—	434 (sh)	—	400	143 (A_g)	
—	178	175	318	118 (B_g)	
—	121	125		86 (B_g)	
—	—	70 (sh)			

In view of the previous discussion of the origin of α, it would seem reasonable to conclude that the O—H vector points along [c], to within our experimental error of 30′. This coincidence is not required by the space group of the crystal, and would not seem to be explained by any hydrogen-bonding interaction between neighbouring OH$^-$ ions; the O . . O distance is long (3.19 Å) and calculations [31,32] of the charge distribution in OH$^-$ put a negative charge on H, in agreement with its high chemical shift.[33] The explanation may lie in the stereochemical requirements of the short hydrogen-bond to the water molecules.   If O—H is parallel to [c], the two H . . O—H angles are 101°31′, which possibly is that value which allows maximum overlap of the hydrogen bonding orbitals.   The non-zero value of η is at first sight governed by the proximity (2.28 Å) of the two Li^+ ions of the shared tetrahedra; however a point-charge model predicts that ϕ_{xx} should lie along the b-axis, in disagreement with experiment.   The value of the OD$^-$ quadrupole coupling constant in LiOD · D_2O at 82 K (271.7 kHz) is significantly lower than that observed [2] in LiOD at 77 K (290.7 kHz).   The former value however requires correction for the effects of lattice modes.
        Turning now to the temperature dependence of the quadrupole coupling constants,

we assume that this will be dominated by the H$_2$O and OD$^-$ torsional modes. Table 3 shows the frequencies observed in the neutron inelastic scattering spectra of LiOH · H$_2$O (and LiOD · D$_2$O) together with infra-red and Raman [15] results.

The most prominent feature of both the energy-loss and energy-gain neutron spectra of LiOH · H$_2$O is a peak at 642 cm^{-1} which is apparently related to a poorly-resolved peak near 468 cm^{-1} in LiOD · D$_2$O (frequency ratio = 1.37).   Assigning the latter to an OD$^-$ torsional mode, ω_t, which is doubly degenerate and of moment of inertia I_t, and using the Bayer equations in the form[34]

$$\langle \theta^2 \rangle = \frac{\hbar}{I_t \omega_t} \left\{ \frac{1}{2} + \frac{1}{\exp(\hbar \omega_t / kT)} \right\},$$ (2)

with

$$\left(\frac{e^2 q Q}{h} \right) = \left(\frac{e^2 q_0 Q}{h} \right)(1 - \tfrac{3}{2} \langle \theta^2 \rangle)$$ (3)

(the change in η being negligible), we calculate that between 82 and 273 K, the deuteron quadrupole coupling constant should diminish by 3.5 kHz, compared with an experimental change of $(271.7-267.9) = 3.8$ kHz; this is reasonable agreement, and supports the spectroscopic assignments.   The " rigid-lattice " value $(e^2 q_0 Q/h)$ is 295 kHz, which is 25 kHz less than the torsionally-corrected value [2] in LiOD(320 kHz).   The mode is infra-red active in LiOH · H$_2$O and is a doublet, the degeneracy being resolved as expected from the structure; it does not appear in the Raman spectrum,[15] in agreement with this assignment.   The H$_2$O modes are not so readily assigned; the strongest feature in the neutron energy loss spectrum above 642 cm^{-1} is a peak at 799 cm^{-1}, and less prominent peaks at 953 and 1011 cm^{-1}, one or more of which appear to correspond to the weak peak at 641 cm^{-1} in the neutron energy-gain spectrum of LiOD · D$_2$O.   We therefore assign the former to the three H$_2$O torsions, the lowest at 799 cm^{-1} being that about the two-fold axis, which is expected to be infra-red inactive and will have A_g symmetry in the Raman spectrum.   The wavenumber of this mode is higher than is often found in other hydrates,[35] which is understandable in view of the strong hydrogen-bonding in LiOH · H$_2$O.   With these assignments, eqn (2) and (3) predict a change in $(e^2 q Q/h)$ between 82 and 273 K of less than 0.4 kHz which (to within experimental error) is consistent with the lack of any change in the experimental values.

[1] Part 5, D. W. Bearfield, M. A. Robb and J. A. S. Smith, *J.C.S. Faraday II*, 1974, **70**, 920.
[2] T. Chiba, *J. Chem. Phys.*, 1967, **47**, 1592; *erratum*, p. 5461.
[3] R. Pepinsky, *Z. Krist.*, 1940, **102**, 119.
[4] H. Rabaud and R. Gay, *Bull. Soc. Franç. Minér. Crist.*, 1957, **80**, 166.
[5] J. L. Sampson and M. A. Di Piettro, *Rev. Sci. Instr.*, 1963, **34**, 1150.
[6] N. F. M. Henry, H. Lipson and W. A. Wooster, *Interpretation of X-ray Diffraction Photographs* (Macmillan, London, 1953), p. 65.
[7] J. Royston and J. A. S. Smith, *Trans. Faraday Soc.*, 1970, **66**, 1039.
[8] N. W. Alcock, *Acta Cryst.*, 1971, **B27**, 1682.
[9] F. N. H. Robinson, *J. Sci. Instr.*, 1959, **36**, 481.
[10] J. Pearson, personal communication.
[11] J. O. Clifford, M. Dixon and J. A. S. Smith, *Chem. Phys. Letters*, 1967, **1**, 185.
[12] P. A. Egelstaff, *Inelastic Scattering of Neutrons* (I.A.E.A., Vienna, 1961), p. 25.

[13] A. J. Leadbetter and M. W. Stringfellow, *Neutron Inelastic Scattering* (I.A.E.A., Vienna, 1972), p. 501.

[14] G. M. Volkoff, H. E. Petch and D. W. L. Smellie, *Canad. J. Phys.*, 1952, **30**, 270; see also J. F. Nye, *Physical Properties of Crystals* (Oxford Univ. Press, London, 1957), p. 165.

[15] E. Drouard, *Compt. rend.*, 1958, **247**, 68; 1959, **249**, 665.

[16] J. Verhoeven, A. Dymanus and H. Bluyssen, *J. Chem. Phys.*, 1969, **50**, 3330.

[17] M. Dixon, T. A. Claxton and J. A. S. Smith, *J.C.S. Faraday II*, 1972, **68**, 2158.

[18] D. Neumann and J. W. Moskowitz, *J. Chem. Phys.*, 1968, **49**, 2056.

[19] S. Aung, R. M. Pitzer and S. I. Chan, *J. Chem. Phys.*, 1968, **49**, 2071.

[20] J. F. Harrison, *J. Chem. Phys.*, 1967, **47**, 2990.

[21] G. P. Arrighini, C. Guidotti and O. Salvetti, *J. Chem. Phys.*, 1970, **52**, 1037.

[22] C. W. Kern and R. L. Matcha, *J. Chem. Phys.*, 1968, **49**, 2081.

[23] L. H. Jones, *J. Chem. Phys.*, 1954, **22**, 217.

[24] Z. M. El Saffar, *J. Chem. Phys.*, 1967, **45**, 4643.

[25] L. W. Reeves, *Progr. Nuclear Magnetic Resonance Spectr.*, 1969, **4**, 193.

[26] G. Ferraris, D. W. Jones and J. Yerkess, *Acta Cryst.*, 1972, **B28**, 209.

[27] J. Almlöf, J. Lindgren and J. Tegenfeldt, *J. Mol. Struct.*, 1972, **14**, 427.

[28] B. Berglund and J. Tegenfeldt, *Mol. Phys.*, 1973, **26**, 633.

[29] B. Pedersen, *Acta Chem. Scand.*, 1968, **22**, 453.

[30] T. Chiba, *J. Chem. Phys.*, 1964, **41**, 1352.

[31] I. D. Campbell and C. K. Coogan, *J. Chem. Phys.*, 1965, **42**, 2738.

[32] J. L. J. Rosenfeld, *J. Chem. Phys.*, 1964, **40**, 384.

[33] R. Grahn, *Acta Chem. Scand.*, 1965, **19**, 153.

[34] T. P. Das and E. L. Hahn, *Nuclear Quadruple Resonance Spectroscopy* (Academic Press, New York, 1958), p. 43.

[35] J. J. Rush, J. R. Ferraro and A. Walker, *Inorg. Chem.*, 1967, **6**, 346.