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The Equilibrium Hydrogen—Hydrogen Distances in the Water Molecules in Potassium and Rubidium Oxalate Monohydrates

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From the proton magnetic-resonance spectra of single crystals of $K_2C_2O_4 . H_2O$ and $Rb_2C_2O_4 . H_2O$ held at room temperature, the equilibrium length, R_e, and orientation of the proton–proton line segments in the water molecules have been determined. The two salts are isomorphous, and the water molecules are situated on the twofold axes making an angle φ_0 with the c axis. The following results are obtained:

$$K_2C_2O_4 . H_2O \qquad R_e = 1 \cdot 5341 \pm 0 \cdot 0030 \text{ Å} \qquad \varphi_0 = 22 \pm 1°$$
$$Rb_2C_2O_4 . H_2O \qquad R_e = 1 \cdot 5474 \pm 0 \cdot 0030 \text{ Å} \qquad \varphi_0 = 26 \pm 1°$$

These results are discussed on the basis of the known crystal structures.

Pake (1948) first detected and analysed the presence of fine structure in the proton magnetic-resonance spectra of hydrate single crystals and powders. He showed that it is possible from the distance between the fine-structure components to calculate the distance between the hydrogen atoms in the water molecules bound in the lattice of the hydrate. Since this classical study the question has existed whether or not it is possible to detect a significant variation in this distance from one hydrate to another, which would indicate variations in the shape of the water molecule. McGrath & Silvidi (1961) concluded, after re-evaluating data on ten different hydrates, that the observed variations were not significant. But later investigations have shown that the distances deduced in earlier studies may include systematic errors due to intermolecular interactions (Holcomb & Pedersen, 1963; Pedersen & Holcomb, 1963), and further that the motion of the water molecules has a large effect on the deduced value of the intramolecular proton–proton distance (Pedersen, B, 1964), invalidating the conclusion of McGrath & Silvidi (1961).

When the effects of the motion were corrected for, Pedersen (1964) found that the equilibrium proton–proton distances deduced from studies of four differ-

ent hydrates and ice, where the necessary data were available, were all equal within the experimental uncertainty $\pm 0 \cdot 01$ Å, and equal to the value observed for an isolated water molecule, $1 \cdot 51$ Å.

In this paper we shall report on a room temperature proton magnetic-resonance study of potassium oxalate monohydrate (KOMH) and rubidium oxalate monohydrate (RbOMH) where a significant difference between the nuclear magnetic-resonance data for the two components has been detected, and where this difference will be interpreted as arising from a significant difference in the equilibrium intramolecular proton–proton distances between the two compounds.

The compounds chosen for this study are isomorphous and ideally suited for a proton magnetic-resonance study for several reasons. The water molecules are located on the twofold axes in the monoclinic structure, and they are all structurally equivalent with all intramolecular proton–proton vectors parallel. The water molecules are well separated from each other, reducing the intermolecular effects to a tolerable minimum. The compounds do not contain any other nuclei with large magnetic moments, in particular no protons other than those situated in the water molecules. It is further fairly easy to grow single crystals

sufficiently large to give a good signal/noise ratio. The reason for choosing an isomorphous pair of compounds is that we hoped that any variation detected could be easier interpreted on the basis of the minor structural differences between the two compounds mainly brought about from the larger size of the rubidium ion compared with the potassium ion.

The distribution of closest neighbors about the water molecules in this structure is unique. Each water molecule is surrounded by two cations and two oxygen atoms from two different oxalate ions in an approximately planar arrangement (Pedersen, B.F., 1964; Chidambaram, Sequeira & Sikka, 1964).

Of the five available alkali metal oxalates only the three heaviest form hydrates. Hendricks (1935) showed that KOMH and RbOMH are isomorphous, but he had no further data for RbOMH. However, Pedersen (B.F., 1965) has determined the positions of all atoms, except hydrogen, from three-dimensional X-ray data for this compound. Caesium oxalate monohydrate is not isomorphous with the other two (Pedersen & Pedersen, 1965).

We shall in this paper first give the theoretical basis for the interpretation of the proton magnetic–resonance spectra. Then we shall show, in greater detail than is usual, how the distance between the fine structure components is derived from the spectra. Finally, the detected difference between the structural information deduced will be discussed on the basis of the model of the motion of the water molecules in KOMH proposed by Paine & McGrath (1964) and the known crystal structures.

Theory

As first shown by Pake (1948) the proton magnetic-resonance spectrum of a hydrate single crystal, where all intramolecular proton–proton vectors are magnetically equivalent, will in general contain two peaks. The distance between the peaks, ΔH, measured in magnetic field units (G), was given by equation (1) by Pake (1948).

$$\Delta H = \frac{3\mu}{R^3}(3\cos^2\theta - 1). \qquad (1)$$

Here R is the length of the intramolecular proton–proton distance, θ the angle between $\mathbf{R}$ and the external magnetic field, and μ the magnetic moment of a proton ($\mu = 14\cdot1042$ Å^3 G).

Recently, Holcomb & Pedersen (1963) have shown that equation (1) is valid only for a system of isolated water molecules. In a real crystal the water molecules are magnetically coupled to each other; the fine-structure components, therefore, have a finite width and a shape which in general is asymmetric. A closer analysis has shown that the distance between the centres of gravity of the two line components is still determined by intramolecular parameters only, as in equation (1), to first order in the intramolecular interactions. ΔH is therefore given by the following equation:

$$\Delta H = \frac{\displaystyle\int_0^\infty h^2\,[g'(h) - g'(-h)]\,dh}{\displaystyle\int_0^\infty h\,[g'(h) - g'(-h)]\,dh}. \qquad (2)$$

Here $g'(h)$ is the spectrum measured with the use of conventional modulation techniques, $h = H - H_0$, where H is the value of the external magnetic field, and H_0 its value in the centre of the spectrum.

Furthermore, as is well known, the water molecules are not static in the lattice, as assumed by Pake (1948), but are executing vibrational motion of different kinds. Pedersen (1964) has shown from a simple model of the motion that proper averaging of equation (1) over the motion leads to the following equation:

$$\Delta H = 0\cdot980\,\frac{3\mu}{R_e^3}\,[3(1 - \langle\theta_x^2\rangle - 2\langle\theta_z^2\rangle))\cos^2\theta + 3(\langle\theta_x^2\rangle$$
$$- \langle\theta_z^2\rangle)\cos^2\gamma - (1 - 3\langle\theta_z^2\rangle)]. \qquad (3)$$

Here R_e is the equilibrium intramolecular proton–proton distance, $\langle\theta_z^2\rangle$ is the mean-square amplitude of the torsional, rigid body vibration of the water molecule about its twofold axis, $\langle\theta_x^2\rangle$, the mean-square amplitude of the rigid body vibration about an axis normal to the plane of the molecule, and γ is the angle between the twofold axis of the molecule and the external field.

In this paper we shall discuss the application of equations (2) and (3) in analysing two sets of proton magnetic-resonance spectra, one set for KOMH and one for RbOMH. Both sets have been obtained by rotating the crystals about an axis parallel to the twofold axis of the water molecule, hence, $\gamma = \pi/2$.

Furthermore, it will be seen that in both cases $\langle\theta_z^2\rangle = \langle\theta_x^2\rangle$. Under these two conditions equation (3) simplifies to

$$\Delta H = 0\cdot980\,[1 - 3\langle\theta_z^2\rangle]\,\frac{3\mu}{R_e^3}(3\cos\theta - 1). \qquad (4)$$

By comparing this equation with equation (1) we can see that they are equal if $3\mu/R^3$ is put equal to $0\cdot980\,[1 - 3\langle\theta_z^2\rangle]\,3\mu/R_e^3$.

Experimental

The potassium oxalate monohydrate used was p.a. purchased from E. Merck, Germany. The rubidium oxalate monohydrate was made from Rb_2CO_3 (purum Fluka AG) and $C_2H_2O_4 . 2H_2O$ (p.a.* E. Merck, Germany).

The crystals were grown from a saturated water solution cooled from about 50 °C to 30 °C or by slow evaporation of a saturated solution at room temperature. Small seed crystals were hung on a 'glass tree' submerged in the solution, and the tree was rotated slowly in the liquid during the growth. The crystals

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* Guaranteed pure.

used were transparent with well developed faces and a volume of $\frac{1}{2}$ to 1 cm³.

The crystals were glued on a Teflon pin about 7 cm long, which was mounted on a goniometer head made out of non-magnetic materials (a factory-adapted Nonius Y-814 goniometer head). The crystals were oriented visually by means of their external shape to a selected orientation within $\pm 1°$. The goniometer was placed on a device enabling us to rotate it about a direction normal to the magnetic field, and the angle of rotation was read on a circular dial 10 cm in diameter.

The proton magnetic-resonance spectra were recorded on a Varian Asc. DP-60 Dual Purpose NMR-spectrometer (V-4302), which is operating at 60 Mc. sec⁻¹, equipped with a 12″ Varian Asc. Magnet (V-4012). The magnetic field was stabilized and swept by means of a 'Fieldial' unit also from Varian Asc. The 'Fieldial' and spectrometer were connected to an X, Y-recorder from Electro Instrument, Model 500 M. The maximum sweep rate used was 0·08 G.sec⁻¹, maximum radio frequency amplitude (H_1): 1 mG and modulation amplitude 0·14 G. The signal/noise was better than 10:1.

Analysis of the spectra

The crystals were always oriented with the monoclinic b axis parallel to the rotation axis which is orthogonal to the magnetic field. In both oxalates the water molecules are sitting on the twofold axes parallel to the b axis. Hence, the angle γ in equation (3) is 90°, and equation (3) can in this case be written:

$$\Delta H = 3a_1 \cos^2 (\varphi_0 - \varphi) - a_2 \qquad (5)$$

where

$$a_1 = 0·98 \frac{3\mu}{R_e^3} (1 - \langle \theta_x^2 \rangle - 2\langle \theta_z^2 \rangle) \qquad (6)$$

and

$$a_2 = 0·98 \frac{3\mu}{R_e^3} (1 - 3\langle \theta_z^2 \rangle) . \qquad (7)$$

Here φ is the angle between the magnetic field and the c axis, and φ_0 the angle between R_e and the c axis. In Fig. 1 are given 19 spectra for $K_2C_2O_4 . H_2O$ obtained by rotating the crystal in steps of 10° from 0 to 180°. The set of spectra used in the analysis was obtained by rotating the crystals in steps of 5° in the same angular interval. Two spectra were recorded at each setting.

To extract ΔH from each spectrum the following procedure was used. Each spectrum was copied on graph paper by drawing a smooth curve through the noise. The centre of the spectrum was marked by a small water peak (omitted from Fig. 1) due to occluded water. Each half of the spectrum was treated in the following way. The ordinate was divided into arbitrary, but equidistant parts, d, such that $x_i = d . i$, and the value of the spectrum, y_i', was read at each x_i. The

value of d was chosen so that the line component was divided into about 25 points. The y_i''s on corresponding points on each half of the spectrum were subtracted, i.e. $y_i = y_i' - y_{-i}'$, giving the y_i's that formed the basis for the further treatment.

The following quantities were then calculated from the experimental values:

$$A_n' = \sum_{i=0}^{m} x_i^n y_i \quad \text{with } n = 0, 1, 2 .$$

It was found that a rather small error in the choice of base line could affect the values of A_n'. If we assume that the chosen base line is parallel to the true base line, this can easily be detected and corrected for. This is due to the fact that if we had chosen the true base line, then A_0' should be zero. It is therefore easy to show that the corrections are

$$A_n = A_n' - \frac{1}{n+1} \cdot x_m^n A_0' .$$

From the values obtained of these A_n's the line splitting, ΔH, can be derived.

$$\Delta H = A_2 / A_1 .$$

The values of ΔH thus deduced were first plotted on graph paper to correct the experimentally determined φ_0 from the positions of the extrema, and then the values of ΔH were fitted analytically to equation (5) by a least-square analysis. The results are:
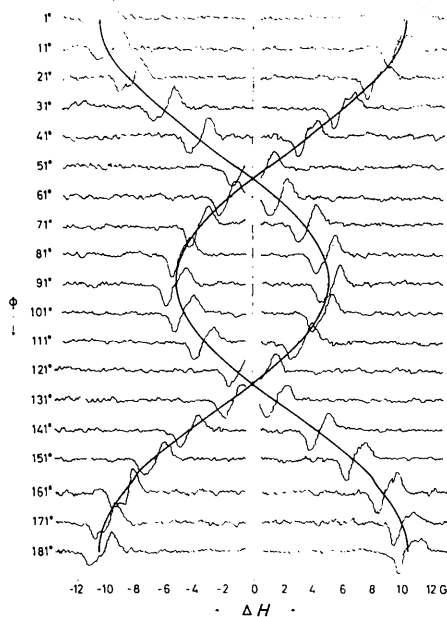

Fig. 1. A set of proton magnetic-resonance spectra of a single crystal of potassium oxalate monohydrate. The b axis of the crystal is always normal to the magnetic field, and φ is the angle between the direction of the magnetic field and the intramolecular proton–proton line in the water molecule. The curves have been drawn from the equation $\Delta H = 10·4$ $(3 \cos^2 \varphi - 1)$.

KOMH:

$a_1 = 10\cdot35 \pm 0\cdot03$ G, $a_2 = 10\cdot41 \pm 0\cdot03$ G,

$\sigma = 0\cdot15$ G, $\varphi = 22° \pm 1°$

RbOMH:

$a_1 = 10\cdot14 \pm 0\cdot03$ G, $a_2 = 10\cdot12 \pm 0\cdot03$ G,

$\sigma = 0\cdot15$ G, $\varphi = 26° \pm 1°$.

σ is the standard deviation in the individual values of ΔH, and the standard deviation in the a's is also given. The individual values of ΔH are given in Figs. 2 and 3, where ΔH is plotted as a function of $\cos^2(\varphi - \varphi_0)$.

Discussion

It follows from the functional form of equation (5) that the deduced value of a_1 will be more susceptible to a deviation between the b axis of the crystal and the actual rotation axis than a_2. It is assumed that this deviation is not more than 2°. The values obtained for a_1 and a_2 for each compound are therefore equal within the experimental uncertainty. The data could therefore be analysed with the same over-all fit on the basis of the simple Pake formula, as has been done earlier (Pedersen & Holcomb, 1963). In the light of the mod-
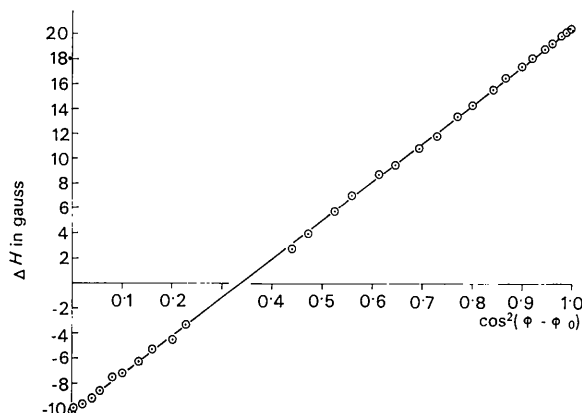

Fig. 2. Observed line splittings in $K_2C_2O_4 . H_2O$ as a function of angular rotation about the b axis.
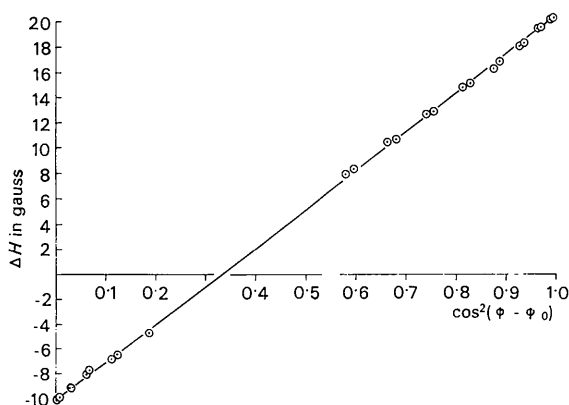
Fig. 3. Observed line splittings in $Rb_2C_2O_4 . H_2O$ as a function of angular rotation about the b axis.

ified equations, however, equations (5), (6), and (7), the equality of a_1 and a_2 tells us that $\langle\theta_x^2\rangle = \langle\theta_z^2\rangle$ for the potassium and rubidium salts at room temperature. Hence, equation (4) is applicable in both cases and we put

$$a_1 = a_2 = \Delta H_0 = 0\cdot98\,\frac{3\mu}{R_e^3}\,(1 - 3\langle\theta_z^2\rangle)\,.$$

The experimental values obtained for ΔH_0 for the two salts seem to be significantly different, as the difference between the two is about ten times the standard deviation. From equation (4) it follows that this difference can either be due to a change in R_e or in $\langle\theta_z^2\rangle$, in going from the potassium to the rubidium salt. In other words, the observed change in the value of ΔH_0 can either be due to a change in the shape, or a difference in the motion of the water molecules in the two isomorphous salts. These two possibilities will now be discussed on the basis of a proton magnetic resonance investigation of KOMH by McGrath & Paine (1964), and the refinement of the crystal structures of KOMH and RbOMH carried out by Pedersen (B.F., 1964) and Pedersen (B.F., 1964, 1965).

McGrath & Paine (1964) have studied the temperature dependence of the proton magnetic-resonance spectrum of a single crystal of KOMH in different orientations relative to the magnetic field. Within the stated, probable error in ΔH_0, $\pm 0\cdot12$ G, they could not observe any variation in ΔH from $-200°C$ to $120°C$ in any of the orientations used. The temperature dependence should be a measure of the temperature dependence of $\langle\theta_z^2\rangle$. $\langle\theta_z^2\rangle$ has been shown earlier to be given by the following equation obtained from a harmonic model of the motion:

$$\langle\theta_z^2\rangle = 0\cdot200\ V^{-0\cdot5}\ (\tfrac{1}{2} + [\exp{(201\ V^{0\cdot5}/T)} - 1]^{-1})\,. \quad (8)$$

Hence, if $\langle\theta_z^2\rangle$ is only slowly changing with temperature, the potential well in which the water molecules are trapped has to be deep, i.e. the value of V has to be large. In earlier studies it has been found that V is equal to the energy of the two hydrogen bonds by which the water molecule is bound by in the lattice, and one should therefore expect in this case, where the oxygen–oxygen distance in the hydrogen bond has the normal value of $2\cdot77$ Å*, that V was about 6 kcal.mole^{-1}, (Holcomb & Pedersen, 1962). But this value inserted in equation (8) would give rise to a much larger variation in $\langle\theta_z^2\rangle$ than observed. McGrath & Paine (1964), however, point out that there are four fairly close cations in the neighbourhood of each water molecule, and that coulomb repulsion between these cations and the hydrogen atoms, assumed to carry a positive charge of 0·33 e, will increase the value of V. A calculation by these authors shows that this effect, calculated on the basis of a simple electrostatic point charge model with each cation carrying a charge $+e$,

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* KOMH: $2\cdot746 \pm 0\cdot011$ Å (Pedersen, B.F., 1964)
  RbOMH: $2\cdot785 \pm 0\cdot019$ Å (Pedersen, B.F., 1965).

will increase V from 6 kcal.mole^{-1} to 14 kcal.mole^{-1}. Such an increase in V will bring down the predicted variation in ΔH_0 from 1·1 G to 0·3 G when the temperature increases from $-200\,°C$ to $+120\,°C$.

If this model is correct one should expect only a minor difference in V between KOMH and RbOMH. The radius of the Rb$^+$ ion is about 0·15 Å larger than the K^+ ion (Slater, 1964), and the shortest K–H distances in KOMH are about 3 Å. Hence, the shortest cation–hydrogen distance is expected to increase about 5% in going from KOMH to RbOMH. As the potential energy is inversely proportional to the distance, the part of the potential, V, due to coulombic repulsion between equal charges, will decrease not more than 5%. Furthermore, because the oxygen–oxygen distances in the hydrogen bonds are found to be equal within the experimental uncertainty in the two salts, the parts of V due to the hydrogen bonds are expected to be the same in the two compounds. Therefore, if V in KOMH is 14·0 kcal.mole^{-1}, V in RbOMH is expected to be reduced to, at most, 13·5 kcal.mole^{-1}. These two values of V have been used to calculate $\langle\theta_z^2\rangle$ in the two salts, and from these values we have calculated the value of the equilibrium intermolecular proton–proton distances; the results of the calculations are given in Table 1.

Table 1. *The equilibrium proton–proton distances in KOMH and RbOMH*

	ΔH_0	$\langle\theta_z^2\rangle$	$3\mu/R_e^3$	R_e
KOMH	10·41±0·03	0·0311	11·72±0·03	1·5341±0·0014
RbOMH	10·12±0·03	0·0320	11·42±0·03	1·5474±0·0014

It follows from the data in Table 1 that the reduction in the value of V from KOMH to RbOMH is not sufficient to make the two values of R_e equal. A simple calculation shows that if R_e in RbOMH were equal to R_e in KOMH it would require a value of V equal to 9·8 kcal.mole^{-1} in RbOMH, which is very much lower than the value estimated for KOMH by McGrath & Paine (1964), 14·0 kcal.mole^{-1}. It is difficult to understand how the small differences in the crystal structures of the two isomorphous compounds can lead to such a substantial difference between the potentials as 4·2 kcal.mole^{-1}.

The uncertainty limits given on R_e in Table 1 are as calculated from the uncertainty in ΔH_0, ±0·03 G. But the accuracy of the derived values of the proton–proton distances depends also, obviously, on the accuracy with which we know the values of V. The standard deviation in V is not known, however, but we will estimate it to be ±1·0 kcal.mole^{-1}, which probably is not too optimistic. This will lead to a standard deviation in R_e of 0·0026 Å, so that the combined uncertainty from both sources, ΔH_0 and V, gives a standard deviation of 0·0030 Å. The observed difference between the values of R_e in RbOMH and KOMH, 0·0133 Å, is therefore 3·1 times the estimated standard deviation of this difference. Hence, according to the

criteria given by Cruickshank (1949), this difference must be regarded as significant. We therefore conclude that the value observed for R_e in KOMH, 1·5341 ± 0·030 Å, is significantly different from the value of R_e in RbOMH, 1·5474 ± 0·0030 Å.

R_e in the isolated water molecule in the gas phase has been found by Benedict, Gailar & Plyler (1956) to be 1·5140 ± 0·0010 Å. Hence R_e in KOMH is 0·0201 Å larger than the gas value, and RbOMH is 0·0334 Å larger, and these, according to the above discussion, must therefore be regarded as highly significant differences. This increase in the value of R_e when the water molecule is bound in the lattice can be understood from inspection of the crystal structures. In both structures the angle between the hydrogen bond acceptor oxygen–water oxygen is larger than the H–O–H angle in the isolated water molecule, 119·7° ± 0·7° in KOMH and 126·2° ± 0·7° in RbOMH compared with 104·52° in the isolated H$_2$O molecule. It is then understandable that R_e is stretched slightly under the influence of the hydrogen bond acceptor atoms, as both the O–H bond length (Lippincott & Schroeder, 1955) and the H–O–H angle are expected to increase in this situation.

The value obtained for R_e in KOMH, 1·5341 ± 0·0030 Å, can be compared with the value obtained by Chidambaram et al. (1964) in their neutron diffraction study, 1·557 ± 0·028 Å. However, the latter result is uncorrected for thermal motion, which also affects the interatomic distances determined from neutron data in a complicated way, as thoroughly discussed by Hamilton (1962).

The validity of the conclusions one can draw from the values obtained for R_e in the two compounds under study, with regard to the configuration of the H$_2$O molecule, is somewhat uncertain, as the equilibrium configuration of this molecule is determined by *two* parameters, and we have determined only one. If we assume, however, that the H–O–H angle is unchanged from the value in the isolated water molecule, 104·52°, as discussed by Chidambaram (1962), we calculate the O–H distance to be 0·970 Å in KOMH and 0·978 Å in RbOMH. These values are slightly smaller than the value found empirically by Hamilton (1962) from neutron diffraction data, when the O–O distance is 2·77 Å: 0·99 Å. As the H–O–H angles in the H$_2$O molecules in KOMH and RbOMH are expected to be larger than the equilibrium value, owing to non-linear hydrogen bonds, these relatively short O–H distances just derived seem to support an earlier theoretical prediction (Chidambaram, 1962; Korst, Savel'ev & Sokolov, 1964) that the H–O–H angle decreases when the H–O bonds are stretched. If this view is correct, R_e might not be very susceptible to configurational changes in the H$_2$O molecule when it is bound in the lattice of a hydrate, as an increase in the O–H length and a decrease in the H–O–H angle will partly compensate each other in affecting the value of R_e. The somewhat surprising results obtained earlier (Pedersen, B., 1964), that the values of

R_e in four different hydrates and ice are all equal within the experimental uncertainty, ± 0.01 Å, and equal to the corresponding distance in the free molecule, should therefore not necessarily mean that the configuration of the H_2O molecule does not change appreciably in these compounds; it might be that the change is such as to lead to an insignificant change in R_e.

The observed angle between the c axis and R_e, φ_0, is somewhat larger in RbOMH, 26°, than in KOMH, 22°. This is in accordance with the crystal structure where the angle between the c axis and the plane determined by the two hydrogen bond acceptors and the water molecule is also larger in RbOMH, 29·5°, than in KOMH, 27°. These results seem to indicate that the water molecule is twisted out of the plane determined by the hydrogen bond acceptors and the water molecule. This conclusion is supported both by the neutron diffraction study of KOMH by Chidambaram et al. (1964), where the same results are obtained, and the model proposed by McGrath & Paine (1964), where this twist is explained as being due to the proximity of the surrounding cations.

Conclusion

The equilibrium proton–proton distance in the water molecule has been found to be 1.5341 ± 0.0030 Å in potassium oxalate monohydrate and 1.5474 ± 0.0030 Å in the isomorphous rubidium oxalate monohydrate from an analysis of the room temperature proton magnetic-resonance spectra of the two salts. The effects of the motion of the water molecule have been corrected for on the basis of a method given by Pedersen (1964) and a model of the motion given by McGrath & Paine (1964). The difference between the two values of the equilibrium distance obtained in the two salts are concluded to be significant, and also significantly different from the value of the corresponding distance in the free molecule, 1.514 Å. The stretching of R_e in the two oxalates is explained on the basis of the known crystal structures, as determined by Pedersen (B.F., 1964, 1965), as resulting from effects of non-linear hydrogen bonds.

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The Structure of Liquid Aluminum–Iron Alloys

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X-ray diffraction measurements have been made on liquid alloys of aluminum containing up to 4 at. % of iron, at temperatures between 760 °C and 1000 °C. The results indicate that the liquids consist of a random array of the two types of atom and do not contain polyhedral structural units of the type found in the intermetallic compounds occurring in the solid phase of these alloys. This conclusion is supported by calculations of the scattering expected from various random and polyhedral models. A detailed fit of observed to calculated scattering cannot be made because of the difficulty of constructing accurate radial distribution functions for a multi-component system.

Introduction

The compounds which are found in aluminum-rich alloys of aluminum with transition metals are char-acterized by very narrow ranges of composition and complicated crystal structures. According to one interpretation (Black, 1956) the significant features of these structures are the polyhedra formed by the arrangements of aluminum atoms around a central transition

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