de retournements moléculaires y est supprimée, mais qu'il subsiste encore une forte agitation anisotrope. L'analyse structurale de la forme III et des traînées de diffusion de la forme II en voie de transformation II → III nous fourniront des informations sur le mécanisme de cette transition.

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The Positions of Protons around Mn^{2+} in $La_2(Mg,Mn)_3(NO_3)_{12}.24H_2O$

By R. DE BEER, W. DE BOER, C. A. VAN'T HOF AND D. VAN ORMONDT

Laboratorium voor Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands

The coordinates of protons in the complex $[Mn(H_2O)_6]^{2+}$ in $La_2Mg_3(NO_3)_{12}.24H_2O$ doped with a small amount of Mn^{2+} have been measured by means of electron nuclear double resonance (ENDOR) at $T=20K$. The accuracy of the method is significantly higher than that of an X-ray diffraction analysis applied to the same type of salt hydrate.

Introduction

The determination of hydrogen atom positions in inorganic crystals by means of X-ray diffraction is not very precise since the scattering power for X-rays of the hydrogen atom is low with respect to that of heavy atoms (Baur, 1972). This is demonstrated clearly in the case of $Ce_2Mg_3(NO_3)_{12}.24H_2O$ (Zalkin, Forrester & Templeton, 1963). Despite the high accuracy of the structure analysis the standard deviation of the hydrogen coordinates was about 0·2 Å. Also, the average intramolecular OH distance was found to be only $r_{OH}=0.72$ Å and the average intramolecular HH distance only $r_{HH}=1.18$ Å, while these values usually are a few tenths of an Å higher in most crystalline hydrates (Reeves, 1969).

A method to improve hydrogen positions obtained by X-ray diffraction has been given by El Saffar (1966). In this method the lengths and the directions of the HH vectors with respect to the crystal axes are determined with proton magnetic resonance. Each of these vectors is then to be assigned to the proper water-oxygen atom in the crystal. This is done by establishing a probable hydrogen-bonding scheme and comparing the resulting HH vectors with those found by means of the magnetic-resonance measurements. The arrangement which gives the best agreement is selected. The shape of the water molecules is fixed by assuming an OH distance of 0·987 Å. Finally the plane in which a water molecule is lying is determined by minimizing the sum of the squares of the distances of the two protons to their respective acceptor atoms.

A crystal of the isomorphic diamagnetic salt $La_2Mg_3(NO_3)_{12}.24H_2O$ has been investigated by proton magnetic resonance (Serra, Lajzérowicz-Bonneteau, Cohen-Addad & Ducros, 1966). For one of the four groups of water molecules [$W1$ according to the nomenclature of Zalkin *et al.* (1963)] present in the lattice r_{HH} was found to be 1.58 ± 0.02 Å, while the corresponding distances in the three remaining groups were near this value. No El Saffar type of analysis was applied however.

In the present study an alternative magnetic-resonance method was used to determine nuclear coordinates, namely that of electron nuclear double resonance (ENDOR) (Baker, Davies & Reddy, 1972; van Ormondt, de Beer, Brouha & de Groot, 1969). It is applicable to diamagnetic substances that can be doped with a small amount of substitutional paramagnetic impurity ions. The substance we investigated was $La_2Mg_3(NO_3)_{12}.24H_2O$, doped with manganous ions at the magnesium sites. In this salt each manganous ion is surrounded by six water molecules. The internal magnetic field caused by the magnetic moment of a manganous ion strongly affects the energy levels of nearby protons. From the observed shifts of the proton resonance lines one can determine the MnH vector, using a formula for the dipolar interaction similar to that applied in the method of El Saffar. As the position of the manganous ion in the crystal is known, that of the proton follows immediately. In this way the coordinates of the protons in the two non-equivalent complexes $[Mn(H_2O)_6]^{2+}$ which occur in the double nitrate salt, could be determined. The protons of the

water molecules that do not belong to a metal–water complex [$W4$ according to the nomenclature of Zalkin *et al.* (1963)] have not been investigated in the present study. However, this would have been feasible since the signals of these protons are clearly visible in the ENDOR spectra (van Ormondt & Visser, 1968).

A complication in the method was that the magnetic interaction between the manganous ion and a proton in the complex is influenced by the intermixing of the manganese and water wave functions. However, it was found that this intermixing could effectively be taken into account by transferring some unpaired electron density from the manganous ion to the oxygen atoms of the neighbouring water molecules. The exact amount of transferred spin density could be inferred from the degree of deviation from cylindrical symmetry of the proton hyperfine tensor. For this correction the position of the oxygen atom lying between the manganous ion and the proton had to be known, of course. In connexion with this another complication arose because of the difference in the size of the magnesium and the manganous ion, the ionic radius of the latter being approximately 0·15 Å bigger (Pauling, 1960). A translation of the oxygen atom by 0·15 Å from its original position was assumed in the calculations. As an indication of the reliability of the method we mention that the HH distance in the same water molecule as investigated by Serra, Lajzérowicz-Bonneteau, Cohen-Addad & Ducros (1966) was found to be 1·57 Å which agrees well with the value mentioned above.

The proton coordinates determined in this investigation have recently been used by Andriessen (1972) in a Hartree–Fock self-consistent field study of the complex [Mn(H$_2$O)$_6$]$^{2+}$. The experimentally observed dependence of the isotropic magnetic hyperfine interaction between the manganous ion and the protons on the orientation of the water molecule in the complex could be qualitatively explained by this author.

Theory

The primitive cell of the double nitrate La$_2$Mg$_3$(NO$_3$)$_{12}$.24H$_2$O contains one formula unit which is built up from five complexes, three [Mg(H$_2$O)$_6$]$^{2+}$ and two [La(NO$_3$)$_6$]$^{3-}$, and six water molecules which do not belong to a particular cation. The manganous ions present as an impurity in the crystal occupy the magnesium sites. In this section the computational method for obtaining the positions of the protons of a complex [Mn(H$_2$O)$_6$]$^{2+}$ in the crystal is treated.

The manganous ion has five unpaired electrons in the 3d shell, which is thus half filled. Consequently, the spatial distribution of the unpaired electrons is spherically symmetric and the values of the resultant spin S and the resultant orbital angular momentum L are $\frac{5}{2}$ and 0 respectively. The electric potential at the manganese site in the double nitrate crystal is not sufficiently strong to alter this situation. As far as the

magnetic interaction between the manganous ion and the surrounding protons is concerned we may then treat the unpaired electron cloud as a magnetic point dipole, $-g\beta S$, located at the position of the manganese nucleus (Laurance, McIrvine & Lambe, 1962). Transfer of unpaired electrons from the manganous ion to the ligands (Andriessen, 1972) slightly invalidates this simple picture, but nevertheless it serves well as a starting point for the calculations. Corrections necessary to take the electron transfer into account will be considered later in this section.

As with El Saffar's n.m.r. method the calculation of nuclear positions is based on the classical formula for the interaction between two magnetic point dipoles μ_1 and μ_2 at positions r_1 and r_2 respectively

$$\mathcal{H}_{12} = \frac{1}{4\pi\mu_0 r_{12}^3} \left\{ \mu_1 \cdot \mu_2 - 3 \frac{(\mu_1 \cdot r_{12})(\mu_2 \cdot r_{12})}{r_{12}^2} \right\}, \quad (1)$$

where $r_{12} = r_2 - r_1$. In the case considered here μ_1 is the magnetic moment of the manganous ion, $-g\beta S$, and μ_2 that of the proton, $g_p\beta_N I$. If the z axis coincides with the line connecting the manganese nucleus and the proton, (1) becomes, in tensor form,

$$\mathcal{H}_{12} = S \cdot \tilde{A}_d \cdot I = (S_x, S_y, S_z) \frac{g\beta g_p\beta_N}{4\pi\mu_0 r_{\text{MnH}}^3}$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}, \quad (2)$$

where r_{12} is replaced by the symbol r_{MnH}. Note that the trace of the tensor $\tilde{A}_d$ is zero and that two principal values are equal, the latter property being due to the cylindrical symmetry with respect to the manganese-proton line. The tensor is reduced to diagonal form since the proton is lying on the z axis.

In general the experimentally determined tensor is not diagonal. After reducing it to this form the manganese to proton distance can be calculated from equation (2):

$$r_{\text{MnH}} = \left\{ \frac{g\beta g_p\beta_N}{2\pi\mu_0 A_{d3}} \right\}^{1/3}, \quad (3)$$

where A_{d3} is the greatest of the three principal values A_{d1}, A_{d2} and A_{d3} of $\tilde{A}_d$. Further, the direction cosines of the manganese–proton line are equal to those of the principal axis of A_{d3} which is known from the diagonalization process. The proton coordinates obtained in this way must then be corrected for the effect of intermixing of the orbitals of the manganous ion and surrounding water molecules. The mixing coefficients have been calculated by Andriessen (1972) for the complex [Mn(H$_2$O)$_6$]$^{2+}$ with a restricted self-consistent Hartree–Fock procedure. These calculations were carried out for three geometric configurations of the complex. One was the so-called symmetric configuration where the overall symmetry is T_h (Griffith, 1964; Nakagawa & Shimanouchi, 1964) (see Fig. 4). The

other two configurations were those occurring in the double-nitrate salt. Symbolically the delocalization of the unpaired electrons can be represented by the following wave function:

$$\psi'_{Mn} = N(\psi_{Mn} + \lambda\psi_{H2O}) ,\qquad(4)$$

where λ is a (small) admixture coefficient and N a normalizing constant. The symbol ψ_{H2O} stands for the various symmetry orbitals of the water molecule, each having a different value of λ. As the water orbitals contain hydrogen functions the unpaired electrons now have a finite density at the protons. Qualitatively the effects of the mixing are the following: first ,the trace of the tensor is no longer zero, second the proton is no longer lying on the principal axis of A_{d3}, third the cylindrical symmetry of the tensor is destroyed. The non-zero trace originates from the usual isotropic Fermi contact term (Abragam & Bleaney, 1970)

$$\mathscr{H}_F = \sum_{i=1}^{5} \frac{2}{3\pi\mu_0} g\beta g_p\beta_N\delta(\mathbf{r}_i - \mathbf{r}_H)\mathbf{s}_i \cdot \mathbf{I} ,\qquad(5)$$

where the summation is over the five unpaired electrons, δ is the Dirac delta function, $\mathbf{r}_i$ the position of unpaired electron i, and $\mathbf{r}_H$ the position of the considered proton. It can be shown (Owen & Thornley, 1966; de Beer, 1971) that in the case of an S-state ion, like Mn^{2+}, the Fermi contact term gives rise to an isotropic tensor, $\tilde{A}_F$, the magnitude of which is proportional to λ^2. The experimentally determined tensor is the sum of $\tilde{A}_F$ and $\tilde{A}_d$. The other two effects are due to

the fact that the distribution of the electronic magnetic moment is no longer spherically symmetric. As a consequence of this the manganous ion can no longer be treated as a point dipole located at the position of its nucleus. In fact, the elements of the dipolar tensor must now be averaged over the orbital part of the extended wave function represented by equation (4).

In the present paper our aim is to determine proton coordinates from the experimental hyperfine tensor. A possible way to do this is to reconstruct the original simple tensor [see equation (2)] which is valid if the electronic magnetic moment is contracted towards the manganese nucleus. In principle the three effects just mentioned should then be evaluated, using appropriate wave functions for the manganese–water complex. However, in view of the complexity of the calculations involved such a procedure would be very time-consuming. Therefore, we have devised a simple alternative method that treats the transfer in a classical way (van Ormondt, de Beer, Brouha & de Groot, 1969).[*] In this model a small amount of magnetic moment $-(g\beta S) \times \delta$ was placed on each of the six oxygen atoms in the complex, while the magnetic moment on the manganous ion was reduced by six times this amount. All moments were treated as point dipoles located at the nuclei of the atoms involved. Fig. 1 shows the situation for a manganous ion and one water molecule of the complex. A reference frame is chosen such that the manganese nucleus lies at the origin, the proton of hydrogen atom H(1) on the z axis and the oxygen nucleus in the yz plane. The water molecule and the manganous ion need not be coplanar. Ignoring the magnetic moments of the five oxygen atoms not shown in the Figure the tensor of the dipolar interaction is

$$\tilde{A}_d = \frac{g\beta g_p\beta_N}{4\pi\mu_0 r_{MnH}^3} \left[\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \times (1 - 6\delta) \right.\qquad(6)$$

$$+ \left. \left(\frac{r_{MnH}^3}{r_{OH}^3}\right)\begin{pmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2}(1 - 3\cos 2\theta) & -\frac{3}{2}\sin 2\theta \\ 0 & -\frac{3}{2}\sin 2\theta & \frac{1}{2}(1 + 3\cos 2\theta) \end{pmatrix} \times \delta \right],$$

where θ is the MnH'O angle and r_{OH} the distance between the considered proton and the oxygen nucleus. It follows from formula (6) that the original dipolar tensor is extended with two small tensors, one being proportional to 6δ and the other to $(r_{MnH}/r_{OH})^3 \times \delta$. As $r_{MnH} \simeq 3r_{OH}$ the latter tensor is the more important of the two. It can be shown that it causes a rotation of the principal axis of A_{d3} about the x axis, away from the oxygen atom, the new axis being denoted by z'. For small values of δ the angle of rotation φ is easily found to be

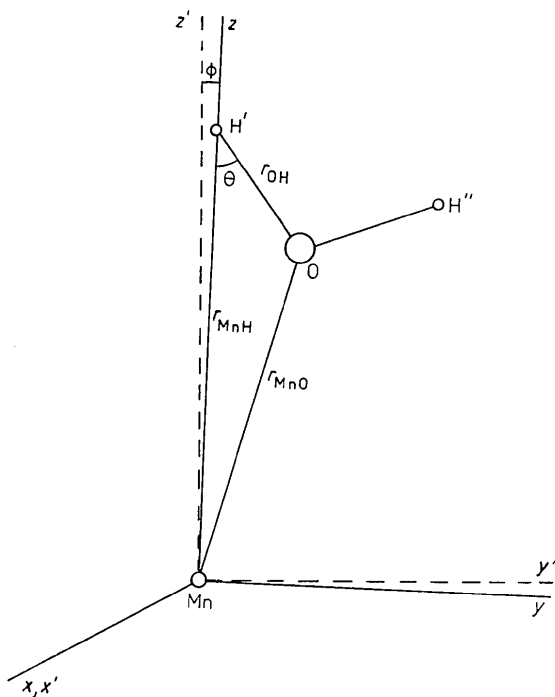$$\varphi = \left(\frac{r_{Mn}}{r_{OH}}\right)^3 \sin\theta \cos\theta \times \delta .\qquad(7)$$

Also, the contributions of the second extra tensor to A_{d1} and A_{d2} are different. If δ is small one finds in first order

$$A_{d2} - A_{d1} = \frac{g\beta g_p\beta_N \sin^2\theta}{4\pi\mu_0 r^3_{OH}} \times 3\delta. \tag{8}$$

Equations (7) and (8) are the basic formulae used for separating the original dipolar tensor from the diagonalized experimental tensor which is expressed in the primed reference frame drawn in Fig. 1. Before carrying out the calculation the isotropic part is removed by subtracting one third of the trace from each of the principal values. An iterative procedure is then followed, starting with δ and φ equal to zero which amounts to assuming that the proton is lying on the principal axis of A_{d3}. First r_{MnH} is calculated from equation (3), which yields approximate proton coordinates and values for r_{OH} and θ. From the latter quantities one obtains δ using equation (8) and then φ using equation (7). The unprimed z axis in Fig. 1 on which the proton is lying is now known and a new value for r_{MnH} can be calculated, this time using equation (6). After this a second iteration cycle is made, which is usually sufficient.

The spin Hamiltonian required for interpreting the ENDOR data was (van Ormondt, de Beer, Brouha & de Groot, 1969).

$$\mathcal{H} = -g_p\beta_N\mathbf{H}.\mathbf{I}+\mathbf{S}.\tilde{\mathbf{A}}.\mathbf{I}+g\beta\mathbf{H}.\mathbf{S}+\mathbf{S}.\tilde{\mathbf{D}}.\mathbf{S} \\ +\mathbf{S}.\tilde{\mathbf{A}}_J.\mathbf{J}, \tag{9}$$

where the first two terms, representing the Zeeman interaction of a proton with the applied magnetic field and the hyperfine interaction with the manganese electrons respectively, are the most important ones (for the ENDOR). The axis of quantization of the electronic magnetic moment is determined mainly by the third term which is the electronic Zeeman interaction. The fourth term represents the interaction of the electrons with the axially symmetric crystal field and the fifth term is the hyperfine interaction between the electrons and the manganese nucleus. The effect of the last two terms is to intermix the electronic spin functions $|M\rangle$ which in turn affects the expectation value of $\mathbf{S}$ in the second term. The method of dealing with these effects has been described by van Ormondt, de Beer, Brouha & de Groot (1969).

Experimental

Crystals of La₂Mg₃(NO₃)₁₂.24H₂O doped with manganese were grown at room temperature from an aqueous solution. The crystals have the shape of a flat hexagonal plate, and are colourless. The ratio of the numbers of manganous ions and magnesium ions in the solution was made equal to 1:3000 by adding the proper amount of manganous nitrate. The manufacturers of the salts used in the solution were: American Potash & Chemical Corp. U.S.A., for La(NO₃)₃.6H₂O, code 549; Merck, Germany, for Mg(NO₃)₂.6H₂O,

p.a.; Noury–Baker, The Netherlands, for a 58·1 wt% aqueous solution of Mn(NO₃)₂.

During the ENDOR measurements the temperature of the samples was maintained at about 20 K° by a cold-helium gas-flow system. The data were collected from many different samples in order to improve the accuracy. Details about the X-band ENDOR spectrometer are given by van Ormondt, de Beer, Brouha & de Groot (1969), and de Beer (1971).

Results and discussion

There are three magnesium sites in the primitive cell of the double nitrate crystal. One site, denoted by I, has C_{3i} symmetry. The remaining two are of the same type and are therefore both denoted by II; they have only C_3 symmetry. Each magnesium ion is surrounded by six water molecules, the oxygen atoms of which lie on the corners of a nearly regular octahedron. Owing to the symmetries just mentioned, there are only two different types of proton in the metal–water complex at site I, H′($W1$) and H″($W1$), and four in a complex at site II, H′($W2$), H″($W2$), H′($W3$) and H″($W3$). The symbols used by Zalkin, Forrester & Templeton (1963) for these hydrogen atoms are H($1W1$), H($2W1$), H($1W2$), H($2W2$), H($1W3$) and H($2W3$) respectively. Table 1 shows the principal values and direction cosines of the principal axes of the hyperfine interaction of the manganous ion with these protons. The contributions to the dipolar part $\tilde{\mathbf{A}}_d$ and the Fermi contact part $\tilde{\mathbf{A}}_F$ have been separated. The signs of the non-diagonal tensor elements in the laboratory reference frame were obtained from comparison with the point dipolar tensor calculated from Zalkin's coordinates. The crystal reference frame used in Table 1 and in succeeding Tables is Cartesian, the length of the unit vector being 1 Å. The x, y and z coordinates in this crystal frame are related to those of Zalkin, Forrester & Templeton (1963) (here denoted by x_Z, y_Z and z_Z) by the transformation

$$x = \frac{\sqrt{3}}{2} x_Z a,$$

$$y = (-\tfrac{1}{2}x_Z + y_Z)a, \tag{10}$$

$$z = z_Z c,$$

where a ($=11\cdot004$ Å) and c ($=36\cdot592$ Å) are the lengths of the axes of the hexagonal unit cell of Ce₂Mg₃(NO₃)₁₂.24H₂O at room temperature. As expected the ratio of the principal values of $\tilde{\mathbf{A}}_d$ is approximately $-1:-1:2$, the deviation from this idealized relation being less than 10% (see Table 1). This result indicates that the point dipolar approximation is a reasonable starting point in the calculation, but that corrections are necessary afterwards.

The manganese-to-proton distances calculated from formula (3) are shown in the first column of Table 2. Assuming that the protons are lying on the principal axis of A_{d3} one then finds approximate coor-

Table 1. *Principal values* (MHz) *of the anisotropic part of the proton hyperfine tensor and corresponding direction cosines* n_x, n_y *and* n_z *of the principal axes expressed in the crystal reference frame defined by equations* (10)

Also given are the values of the isotropic proton hyperfine interaction. The standard deviations are given in parentheses. $T = 20°K$.

		n_x	n_y	n_z
H'(W1)				
A_{d1}	−3·606 (8)	0·782 (6)	0·329 (9)	−0·530 (3)
A_{d2}	−3·300 (8)	−0·572 (9)	0·714 (6)	−0·403 (4)
A_{d3}	6·906 (2)	0·246 (5)	0·618 (2)	0·746 (0)
A_F	0·890 (2)	—	—	—
H''(W1)				
A_{d1}	−3·730 (8)	−0·998 (22)	−0·023 (27)	0·064 (86)
A_{d2}	−3·470 (11)	0·068 (90)	−0·298 (47)	0·952 (9)
A_{d3}	7·200 (4)	−0·002 (8)	0·955 (1)	0·298 (1)
A_F	0·890 (3)	—	—	—
H'(W2)				
A_{d1}	−3·704 (12)	0·603 (15)	0·703 (13)	0·377 (9)
A_{d2}	−3·387 (9)	0·511 (12)	−0·704 (17)	0·494 (6)
A_{d3}	7·091 (9)	0·612 (1)	−0·105 (6)	−0·784 (0)
A_F	0·931 (6)	—	—	—
H''(W2)				
A_{d1}	−3·985 (22)	−0·609 (52)	0·039 (52)	−0·792 (23)
A_{d2}	−3·650 (25)	0·524 (42)	0·770 (42)	−0·362 (52)
A_{d3}	7·635 (16)	0·595 (6)	−0·637 (6)	−0·490 (1)
A_F	0·648 (13)	—	—	—
H'(W3)				
A_{d1}	−3·850 (61)	−0·144 (50)	0·912 (74)	−0·384 (144)
A_{d2}	−3·549 (61)	−0·316 (52)	0·326 (147)	0·891 (27)
A_{d3}	7·399 (21)	0·938 (3)	0·250 (9)	0·241 (3)
A_F	0·661 (16)	—	—	—
H''(W3)				
A_{d1}	−3·340 (24)	−0·221 (71)	−0·628 (82)	0·746 (23)
A_{d2}	−3·190 (11)	0·788 (62)	−0·566 (59)	−0·242 (65)
A_{d3}	6·530 (24)	0·574 (6)	0·535 (6)	0·620 (1)
A_F	1·199 (15)	—	—	—

dinates. The intramolecular proton–proton distances evaluated from these coordinates are listed in the third column of Table 2. It can be seen that at this stage of

the calculation the protons in a water molecule are too far apart, considering the n.m.r. result, $r_{HH} = 1·58 \pm 0·02$ Å for $W1$, mentioned in the Introduction. The situation can be improved by allowing for transfer of some magnetic moment from the manganous ion to the oxygen atom, which brings about a rotation of the principal axis of A_{d3}, as was shown earlier. In order to carry out this procedure the oxygen positions must be known, since values for the MnHO angle θ and the oxygen to hydrogen distance r_{OH} (see Fig. 1) are needed in equations (7) and (8). The ionic radius of Mn^{2+} exceeding that of Mg^{2+} by about 0·15 Å (Pauling, 1960), one then has to take a local distortion around the manganous ion into account. As it is difficult to predict in which direction the oxygen atoms will be displaced we simply applied a radial translation, thereby increasing the metal–oxygen distance from about 2·06 to 2·20 Å. [For comparison we mention that in $MnCl_2.4H_2O$ the average value of the MnO distance is 2·206 Å (Zalkin, Forrester & Templeton, 1964)]. The amount of transferred magnetic moment δ and the resulting rotation φ of the principal axis of A_{d3} calculated with the corrected oxygen position are listed in columns 8 and 9 respectively of Table 2. Although δ is seen to vary considerably within a water molecule, the average value for each molecule appears to be almost the same. This result is not very surprising since the covalency is not expected to vary much from one manganese–water complex to another (Andriessen, 1972). The angles φ were calculated from the average values of δ.

The final values of r_{IIII}, r_{OII} and angle HOH obtained after several iteration cycles (as described in the theoretical section) are listed in columns 4, 6 and 10 respectively. As a result of the transfer of magnetic moment, r_{HH} of $W1$ has now been reduced to the n.m.r. value to within experimental accuracy. The shape of water molecule $W3$ turned out to be rather asymmetric. This may indicate that on substituting Mn^{2+} for Mg^{2+} the oxygen atom of this molecule is displaced not only

Table 2. *The interatomic distances* (Å) *of* r_{MnH}, r_{HH} *and* r_{OH}, *and the* HOH *angles in the complex* $[Mn(H_2O)_6]^{2+}$ *in* $La_2(Mg, Mn)_3(NO_3)_{12}.24H_2O$ *at* $T = 20°K$

The values in columns 5, 7 and 11 are for $[Mg(H_2O)_6]^{2+}$ in $Ce_2Mg_3(NO_3)_{12}.24H_2O$ at room temperature, as determined by neutron diffraction (Hamilton, 1972). The quantities δ and φ in columns 8 and 9 are the amount of transferred magnetic moment and the resulting rotation of two of the eigenvectors respectively. The standard deviations are given in parentheses.

	r_{MnH}*	r_{MnH}†	r_{HH}*	r_{HH}†	r_{HH}§	r_{OH}†	r_{OH}§	δ	φ	∠HOH	∠HOH§
H'(W1)	2·84	2·844 (1)				0·95 (1)	0·97	0·0027 (2)	1·8 (2)°		
H''(W1)	2·80	2·808 (1)				0·96 (1)	0·91	0·0021 (2)	1·7 (1)		
W1‡	2·82	2·826	1·73	1·57 (2)	1·57	0·96	0·94	0·0024	1·8	112°	113°
H'(W2)	2·81	2·818 (2)				0·99 (2)	0·97	0·0028 (3)	1·9 (2)		
H''(W2)	2·75	2·741 (4)				0·96 (4)	0·90	0·0023 (6)	1·6 (5)		
W2‡	2·78	2·780	1·69	1·55 (3)	1·49	0·98	0·94	0·0025	1·8	106	105
H'(W3)	2·77	2·767 (6)				1·12 (6)	1·05	0·0031 (9)	1·4 (5)		
H''(W3)	2·89	2·928 (8)				0·86 (5)	0·83	0·0019 (13)	1·8 (1·0)		
W3‡	2·83	2·848	1·70	1·56 (4)	1·47	0·99	0·99	0·0025	1·6	104	103

* Before correction for transfer of magnetic moment.
† After correction for transfer of magnetic moment.
‡ Average value for the two protons, except in columns 3, 4, 5, 10 and 11.
§ Neutron-diffraction results for $Ce_2Mg_3(NO_3)_{12}.24H_2O$ at room temperature.

radially, but also laterally. On the other hand, asymmetric water molecules do occur in crystalline hydrates (see for instance Verbist, Hamilton, Koetzle & Lehmann, 1972), and therefore it seems impossible to improve on our original estimate of the distortion using the difference between the two values for r_{OH} in a water molecule as a criterion. Moreover, preliminary results obtained by Hamilton (1972) from neutron-diffraction measurements with $Ce_2Mg_3(NO_3)_{12}.24H_2O$ (at room temperature) show the same trend with regard to the shape of the water molecules.* Values for r_{HH}, r_{OH} and angle HOH calculated from Hamilton's coordinates are listed in columns 5, 7 and 11 respectively of Table 2. It follows from the neutron diffraction results that molecule $W3$ is already rather distorted before Mg^{2+} is replaced by Mn^{2+}.

The coordinates of the individual protons determined by means of ENDOR and X-ray diffraction are given in Table 3. The relation between the reference frame used for this table and that used by Zalkin et al. (1963) is given by equations (10). When reading the Table it should be kept in mind that the coordinates determined in this work are for protons near an impurity ion that causes local distortion. We have not ventured to estimate the displacement of the protons as we did for the oxygen atom, because the lateral component of the displacement of the protons is probably more significant than that of the oxygen atoms. However, we have been able to identify in the ENDOR spectrum of site I the lines of a proton $H'(W2^i)$ belonging to a nearby complex $[Mg(H_2O)_6]^{2+}$. (The lines of many other 'far' protons are visible in the spectra. However, the spectra are so complicated that a complete analysis would be very time-consuming.) Therefore it was possible to determine the position of a proton in an undistorted complex. The accuracy of such a calculation is, of course, not very high since the appropriate vector connecting site I and the particular site II to which $H'(W2^i)$ belongs must be known precisely for $T = 20°K$. In order to be able to determine the wanted vector we assumed that the atomic coordinates in

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* These results are preliminary and will be refined by means of computer analysis later. The errors in the protein coordinates are ±0·05 Å.

$La_2Mg_3(NO_3)_{12}.24H_2O$ are exactly equal to those in $Ce_2Mg_3(NO_3)_{12}.24H_2O$. Also we assumed that the coefficients of thermal expansion, parallel and perpendicular to the c axis of the double nitrate crystal (Lebesque, 1973), can be used for calculating the distance between two metal sites as a function of the temperature. A favourable circumstance was the absence of covalency effects, the measured hyperfine tensor having the same properties as that in equation (1) within experimental accuracy. The result of the calculation is given in Table 4. In view of the assumptions required to obtain these coordinates an estimate of the accuracy is very difficult and therefore no errors are given. For comparison the coordinates of the same type of proton near Mn^{2+} are also listed. It can be seen that the magnitude of the displacement of the proton due to the greater radius of the manganous ion as measured with ENDOR, is essentially correct.
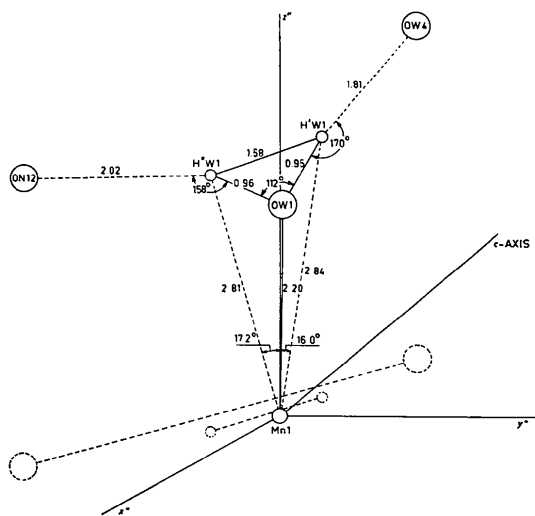

Fig. 2. One of the six water molecules $W1$ near Mn^{2+} at site I in $La_2(Mg,Mn)_3(NO_3)_{12}.24H_2O$. The reference frame is chosen such that the c axis is parallel to the [$\overline{1}11$] direction. Also shown are the oxygen atoms which are involved in the hydrogen-bonding scheme, with their projections on the $x''y''$ plane (indicated with dashed lines). The positions of the other water molecules in the complex follow from rotation about the c axis through ±120° and an inversion.

Table 3. *Proton coordinates* (Å) *in* $La_2(Mg,Mn)_3(NO_3)_{12}.24H_2O$ *as determined by ENDOR at* $T \simeq 20°K$, *and in* $Ce_2Mg_3(NO_3)_{12}.24H_2O$ *as determined by X-ray diffraction* (*Zalkin et al.*, 1963) *at room temperature*

The crystal reference frame is defined by equations (10). The standard deviations are given in parentheses.

Proton	ENDOR			X-rays		
	x	y	z	x	y	z
$H'(W1)$*	0·65 (2)	1·82 (1)	2·08 (0)	0·53	1·85	1·81
$H''(W1)$*	0·00 (3)	2·65 (1)	0·92 (1)	−0·06	2·31	0·96
$H'(W2)$†	1·77 (1)	−0·36 (2)	−2·16 (1)	1·68	−0·42	−1·61
$H''(W2)$†	1·67 (2)	−1·69 (3)	−1·37 (1)	1·57	−1·50	−1·05
$H'(W3)$†	2·57 (1)	0·71 (3)	0·73 (2)	2·23	0·89	0·94
$H''(W3)$†	1·75 (4)	1·51 (4)	1·79 (2)	1·35	1·28	1·57

* z coordinates with respect to site I.
† z coordinates with respect to site II.

Table 4. *Coordinates (Å) of a 'far' proton, $H'(W2^i)$ in $[Mg(H_2O)_6]^{2+}$ determined by ENDOR*

The coordinates of the same type of proton in a manganese complex are also given for comparison.

$H'(W2^i)$	x	y	z	r
Mg^{2+} complex	1·70	−0·29	−1·96	2·61
Mn^{2+} complex	1·77	−0·36	−2·16	2·82

Figs. 2 and 3 show the positions of the protons in the crystal. The positions of the atoms outside the complex $[Mn(H_2O)_6]^{2+}$ were assumed to be insensitive to the presence of the impurity. The reference frames were chosen such that the situations resemble that in Fig. 4, which shows the geometry of a free complex possessing T_h symmetry (Griffith, 1964; Nakagawa & Shimanou-

Fig. 4. The geometry of a free $[Mn(H_2O)_6]^{2+}$ complex. One of four different trigonal symmetry axes is indicated.

Fig. 3. One water molecule $W2$ and one water molecule $W3$ near Mn^{2+} at site II in $La_2(Mg,Mn)_3(NO_3)_{12}$ $24H_2O$. The reference frame is chosen such that the c axis is parallel to the $[\bar{1}11]$ direction. Also shown are the oxygen atoms which are involved in the hydrogen bonding scheme, with their projections on the $x''y''$ plane (indicated with dashed lines). The positions of the other water molecules in the complex follow from rotations about the c axis through $\pm120°$.

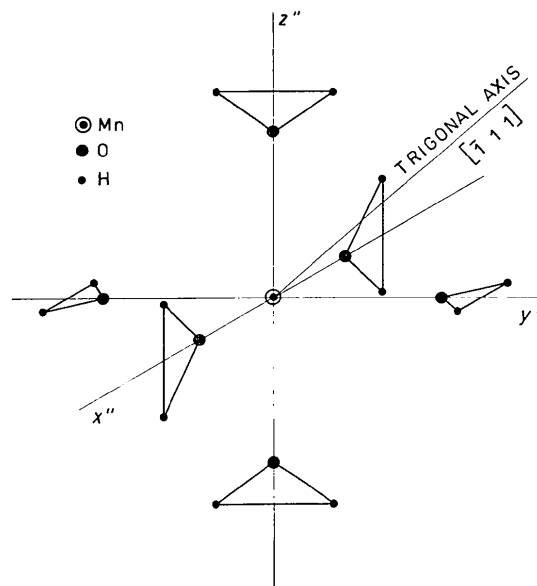chi, 1964). Especially in the case of site I one can see clearly that the water molecule has been twisted by the hydrogen bonds. Without the forces excercised by these bonds the HH vector would have been parallel to either the x or the y axis.

In conclusion we remark that the ENDOR method can be successfully applied to the measurement of the coordinates of a magnetic nucleus lying in the neighbourhood of a paramagnetic impurity ion in a single crystal. In the present case it was possible to correct for the effects of the spreading of the electronic magnetic moment over the ligands of the impurity ion due to covalency and overlap.

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A Variant of the NaCl Structure Type: BaSnS2*

BY J. E. IGLESIAS† AND H. STEINFINK

Materials Science Laboratories, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

A structural analysis based on three-dimensional X-ray data has been carried out for $BaSnS_2$. The space group is $P2_1/c$, $a = 6.0848$ (3), $b = 12.1396$ (8), $c = 6.2356$ (2) Å, $\beta = 97.058$ (4)°. The least-squares refinement of the parameters gave $R = 0.0574$ for 1049 intensities. The structure is a distortion of the NaCl structure and can be considered as a composite of the BaS and SnS structures, both of which are based on the NaCl motif. Ba is in sixfold coordination in a slightly distorted octahedron. Sn is in a distorted octahedral void but is very close to a triangular face of S ions so that it is bonded to 3 sulfur atoms only. In this polar arrangement Sn can be considered to have a tetrahedral environment in which a lone pair of electrons occupies one vertex. The cations are ordered so that Ba layers alternate with Sn layers in the overall NaCl type architecture.

Introduction

Several ternary sulfides containing Ba and Sn have been recently reported (Hervieu, Perez & Hagenmuller, 1967; Susa & Steinfink, 1971; Yamaoka & Okai, 1970; Jumas, Ribes, Philippot & Maurin, 1971). As a result of an attempt to prepare substitutional solid solutions in the Ba–Fe–Sn–S system, we became interested in the crystal structure of one of the possible end members of the series, $BaSnS_2$. $BaSnS_2$ has been prepared by Hervieu, Perez & Hagenmuller (1967), hereafter referred to as HPH. They found the compound to be a black powder with an orange-red color upon grinding. The powder pattern (reported also on card 20–150 of the Joint Committee on Powder Diffraction Standards) was indexed in terms of an orthorhombic lattice with parameters $a = 12.000$ (4), $b = 8.381$ (8), $c = 4.606$ (10) Å with systematic absences compatible with the space

groups *Pnma* and *Pn2$_1$a*. No indication is given as to how the standard deviations of the lattice parameters were estimated but it is unusual that the c axis, which is the shortest, has the greatest standard deviation, a result not common when least-squares refinement of parameters is employed.

Experimental

Since HPH report that the same powder pattern is obtained for $BaSnS_2$ prepared at 800°C or at 650°C, and that long annealing at 650°C failed to indicate any low-temperature modification, we prepared the material from a 1:1 mixture of BaS and SnS fired at 750°C for two weeks, cooling it by cutting off power to the furnace. The material appeared as yellow–orange plate-like crystals with some metallic luster. The main peaks in the powder pattern approximately matched those in the pattern reported by HPH. Several single crystals were selected and oscillation, zero and upper-level Weissenberg and zero-level precession photographs were taken. The diffraction symmetry observed was $2/m$ and the systematic absences were $h0l$, $l = 2n + 1$