JOURNAL OF SOLID STATE CHEMISTRY **38**, 181–185 (1981)

Deuteron Magnetic Resonance and Hydrogen Bond Network of Ammonium Trihydrogen Selenite

I. S. VINOGRADOVA

L. V. Kirensky Institute of Physics Academy of Sciences USSR, Siberian Branch Krasnoyarsk, 660036, USSR

Received June 2, 1980; in final form November 12, 1980

The DMR spectra of single-crystal $ND_4D_3(SeO_3)_2$ have been studied. The principal values and the direction cosines of the field-gradient tensor of deuterons located on three nonequivalent O · · · O hydrogen bonds have been determined. The lengths of hydrogen bonds have been calculated from *eQq/h* values; the deuterons have been located on hydrogen bonds. The comparison with the DMR data of isomorphous compound $RbD_3(SeO_3)_2$ was made; the influence of N–H · · · O hydrogen bonds on the structural parameters O · · · O hydrogen bonds is discussed.

The space group and the heavy-atom structure of ammonium trihydrogen selenite $NH_4H_3(SeO_3)_2$ (ATHS) are the same as those of the isomorphous compound $RbH_3(SeO_3)_2$ (RTHS); however, the physical properties of these crystals are different. RTHS is a ferroelectric below − 115°C, whereas ATHS is a linear dielectric [*1*]. It is of interest to compare these two structures. As follows from the X-ray and neutron diffraction studies [*2, 3*], the unit cells of both crystals consist of NH_4^+ or Rb^+ ions, $HSeO_3^-$ ions, and H_2SeO_3 molecules, and there are three different O · · · O hydrogen bonds which connect via the SeO_3 groups. The parameters of these bonds in RTHS and ATHS (their lengths and spatial arrangement) are very similar, but additional hydrogen bonds N–H · · · O are formed on substitution of NH_4^+ for Rb^+. These new bonds have a great influence both on the O · · · O hydrogen bond system and on the dielectric properties of the crystal. The study of deuteron magnetic resonance (DMR) spectra of single crystals of $ND_4D_3(SeO_3)_2$ was undertaken to obtain detailed information on the hydrogen bond system. The structural parameters of the O · · · O hydrogen bonds were determined, the deuterons were located on these bonds, and a comparison with the DMR data for $RbD_3(SeO_3)_2$ (RTDS) [*4*] was made.

Three single-crystal specimens were provided for experiments. Deuteron magnetic resonance spectra were recorded at 8.8 MHz by rotating the crystals in a magnetic field about three mutually orthogonal axes $X \| a$, $Y \| b$, $Z \| c$ (*a,b,c* correspond to [*3*]). The rotation patterns about the *b* and *c* axes are given in Fig. 1. The principal values and direction cosines of the field-gradient tensor, the values of the quadrupole coupling constant, and the asymmetry parameter of deuterons located on the O · · · O bonds were determined from the angular dependences of quadrupole splitting of the DMR spectra using the Volkoff method [*5*]. The lengths of three O · · · O hydrogen bonds: O(1) · · · O(5), O(2) · · · O(6),

0022-4596/81/080181-05$02.00/0

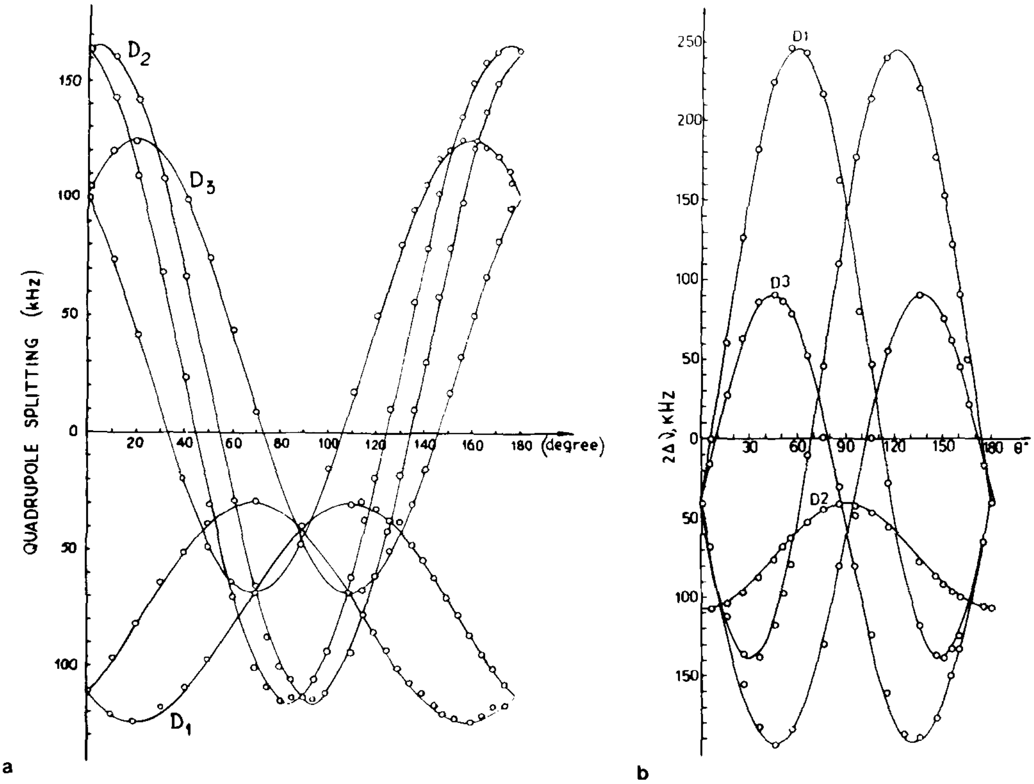

FIG. 1. Rotation patterns of the DMR absorption lines of $ND_4D_3(SeO_3)_2$ at room temperature: (a) – $H_0 \perp b$, $\Theta = \angle c, H_0$; (b) – $H_0 \perp c$, $\Theta = \angle a, H_0$.

TABLE I

DEUTERON QUADRUPOLE COUPLING CONSTANTS eQq/h, ASYMMETRY PARAMETERS η, THE HYDROGEN BOND LENGTHS, AND THE ASSIGNMENTS OF THE FIELD-GRADIENT TENSORS TO HYDROGEN BOND NETWORK[a]

	eQq/h (kHz)	η	$R(O\cdots O)$ Å		φ_z	φ_v	Assignments
			X-Ray	DMR			
D(1)	172.5 ± 1	0.08	2.648	2.606	1	2 45	O(1)–D · · · O(5) O(5)–D · · · O(1)
D(2)	156.0 ± 1	0.12	2.608	2.562	0	22 3	O(6)–D · · · O(2) O(2)–D · · · O(6)
D(3)	145.5 ± 1	0.17	2.546	2.539	7	9 18	O(3)–D · · · O(4) O(4)–D · · · O(3)

[a] Angles φ_z—between the q_{zz} directions and that calculated from structure O–H directions; angles φ_v—between the q_{vv} directions and that calculated normal to the Se–O · · · O plane directions.

O(3) · · · O(4) were calculated from values of the quadrupole coupling constant eQq/h by a method developed by Chiba [6] (the indices 1–6 correspond to [3]). Each field-gradient tensor was related to the specific hydrogen bond (Table I) since the q_{zz} direction is nearly parallel to the direction of the O–D (O–H) bond. So far as q_{yy} is nearly perpendicular to the Se–O · · · O plane, the localization of the deuterons on the hydrogen bonds near concrete oxygen atoms was made from the analysis of the angles φ_y between the q_{yy} direction and the normal to the Se–O · · · O plane.

For hydrogen bonds O(1) · · · O(5) and O(6) · · · O(2) the analysis of φ_y angles shows that their deuterons are ordered and covalently bonded to O(1) and O(2) (Table I). For the third hydrogen bond O(3) · · · O(4) there is a large difference in the directions of the q_{zz} and O–H vector, and correlation of the φ_y angles shows partial disordering of the deuterons with unequal distribution over two possible sites. Data given in Table I are evidence of isostructural hydrogenous and deuterated crystals of trihydrogen ammonium selenite.

Further, comparison between the DMR data in the crystals RTDS and ATDS was made. The values q_{zz} and q_{yy} and their directions in the unit cell were analyzed. q_{zz} is connected with the length and spatial arrangement of the hydrogen bond, q_{yy} characterizes the potential surface of the hydrogen bond. As follows from Table II, the spatial arrangement of hydrogen bonds differs little in the unit cells of RTDS and ATDS crystals (in values of the α_z angles). The lengths of the O · · · O bonds in the ammonium compound are larger than those in the rubidium compound. This lengthening is connected with N–H · · · O bond formation.

Hydrogen bonds for both crystals are shown schematically in Table III. The data for N–H · · · O bonds are taken from [3]. The additional interaction N–H · · · O affects each O · · · O bond in various ways and leads to different effects. Thus, for example, for hydrogen bonds O(1) · · · O(5) in the ammonium compound, both oxy-

TABLE II

THE PRINCIPAL VALUES AND DIRECTION COSINES OF THE DEUTERON EFG TENSORS IN $RbD_3(SeO_3)_2$ AND $ND_4D_3(SeO_3)_2$ SINGLES CRYSTALS[a]

Hydrogen bonds	$ND_4D_3(SeO_3)_2$				$RbD_3(SeO_3)_2$			
	eQq_{ii}/h (kHz)	Direction cosines			eQq_{ii}/h (kHz)	Direction cosines		
		X	Y	Z		X	Y	Z
O(1) · · · O(5)	79.00	+0.0080	+0.9296	−0.3684	79.31	+0.0025	+0.9287	−0.3707
$\alpha_z = 1°$	93.50	−0.5322	+0.3158	+0.7855	90.19	−0.5198	+0.3179	+0.7929
$\alpha_y = 1.5°$	172.50	+0.8466	+0.1898	+0.4972	161.58	+0.8543	+0.1907	+0.4835
O(3) · · · O(4)	60.14	−0.6679	−0.0879	+0.7390	49.33	−0.5977	−0.2591	+0.7587
$\alpha_z = 3°$	85.38	−0.2651	+0.9559	−0.1258	72.70	−0.4175	+0.9084	−0.0187
$\alpha_y = 11°$	145.52	+0.6954	+0.2800	+0.6618	122.03	+0.6844	+0.3279	+0.6512
O(6) · · · O(2)	68.58	−0.4185	+0.1580	+0.8943	65.27	−0.5863	+0.2348	+0.7753
$\alpha_z = 5°$	87.46	+0.7794	−0.4430	+0.4430	83.42	+0.6309	−0.4679	+0.6188
$\alpha_y = 13°$	156.04	+0.4662	−0.8825	+0.0622	148.69	+0.5081	+0.8519	+0.1262

[a] α_z—angles between the q_{zz} directions in both crystals; α_y—angles between the q_{yy} directions in both crystals.

TABLE III

HYDROGEN BOND SYSTEM IN THE CRYSTALS $RbH_3(SeO_3)_2$ AND $NH_4H_3(SeO_3)_2$

$RbH_3(SeO_3)_2$		$NH_4H_3(SeO_3)_2$	
O(1)–H(1) · · · O(5)		. . · O(1)–H(1) · · · O(5)	
	N–H(4)		· · · H(5)–N
O(6)–H(2) · · · O(2)		. . · O(6) · · · H(2)–O(2)	
	N–H(6)		
O(3)–H(3) · · · O(4)		O(3)–H(3) · · · O(4)	
			· · · H(4)–N

gen atoms O(1) and O(5) take part in formation of N–H · · · O bonds as acceptors. Such additional interaction almost does not change the spatial arrangement and potential surface of these bonds in comparison with the rubidium compound (Table II, the angles α_z and α_y characterize the difference in the orientations q_{zz} and q_{yy} in both crystals).

For the O(6) · · · O(2) bonds, upon substitution of NH_4^+ for Rb^+ additional N–H(6) · · ·O(6) bonds are formed, but in this case the additional perturbation affects only O(6) i.e., the donors hydrogen bonds O(6) · · · O(2) in RTHS, but does not affect O(2). This interaction leads to movement of H(2) or D(2) from one side of the bond to the other, resulting in a marked difference in the directions of q_{yy} in both crystals (13°, Table II). In the ammonium compound, H(2) is covalently bonded to O(2) forming a hydrogen bond O(2)–H(2) · · · O(6) (Table I); in the rubidium compound, H(2) is bonded to O(6) giving a bond O(2) · · · H(2)–O(6) ([*4*], Table III).

For the O(3) · · · O(4) hydrogen bonds, substitution of NH_4^+ for Rb^+ results in formation N–H(4) · · · O(4) bonds, and the additional perturbation affects only O(4), i.e., the acceptors of hydrogen bonds O(3) · · · O(4) in RTHS. In this case, in the crystals of ATHS, the shift H(3) along the bond does not take place in comparison with the rubidium compound. From the DMR data the spatial arrangement in this bond changes little, by 3°, in comparison with RTHS. Its potential surface also changes since the q_{yy} direction changes by 11°. However, correlation of the φ_y angles for the O(3) · · · O(4) bond (Table I) does not permit one to make a simple choice between an ordered or disordered arrangement of deuterons D(3) nor to localize exactly their near-oxygen atoms O(3) or O(4). From X-ray and neutron diffraction data, it follows that protons H(3) are ordered and localizing them according to the lesser φ_y angle near O(3) does not contradict the diffraction data. But correlation of the φ_y angles is rather close to the disordering situation when the D(3) are unequally distributed over two possible sites in this bond with their primary localization near O(3). So far as this conclusion disagrees with the diffractional data, it is necessary to specify the state of H(3) protons possibly by other methods.

The analysis of the DMR data together with the diffractional studies data [*3*] shows that formation of the N–H · · ·O hydrogen bonds in ATHS has little influence on the spatial arrangement of O · · · O bonds, but changes their potential surface and, in this way, the electrical properties of the crystal.

References

1. L. A. SHUVALOV, N. R. IVANOV, N. V. GOR-

DEEVA, AND L. F. KIRPICHNIKOVA, *Sov. Phys. Crystallogr.* **14**, 554 (1970).

2. R. TELLGREN, D. AHMAD, AND R. LIMINGA, *Chem. Scripta* **2**, 215 (1972).
3. R. TELLGREN AND R. LIMINGA, *Acta Crystallogr. Sect. B* **30**, 2497 (1974).
4. I. S. VINOGRADOVA AND A. I. ROSLYAKOV, *Sov. Phys. Crystallogr.* **24**, 284 (1979).
5. G. M. VOLKOFF, H. E. PETCH, AND D. W. L. SMELLIE, *Canad. J. Phys.* **30**, 270 (1953).
6. T. CHIBA, *J. Chem. Phys.* **41**, 1352 (1964).