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Deuteron Magnetic Resonance Study of Single Crystals of $NaDSeO_3$

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A deuteron magnetic resonance study of a single crystal of $NaDSeO_3$ at room temperature is reported. The observed electric field gradient tensors correspond to two nonequivalent hydrogen bonds. The quadrupole coupling constants (eQq/h) and asymmetry parameters (η) are found to be 172.8 and 0.07 kHz for D(1), and 152.5 and 0.08 kHz for D(2). D(2) are ordered, but D(1) are found to be dynamically disordered. The DMR results are consistent with recent X-ray reinvestigation. No phase transitions have been encountered in the temperature range 336 to 77 K.

Introduction

Sodium hydrogen selenite belongs to the little known family of $MeHSeO_3$ compounds, namely the alkali-metal hydrogen selenites. The unit cells of hydrogen selenites contain alkali ions, selenite ions, and hydrogen bonds, similar to those of the well-known and well-studied trihydrogen selenites $MeH_3(SeO_3)_2$, which are compounds with interesting physical properties. Therefore, the study of crystal structures (especially the hydrogen bond system and proton dynamics), as well as the occurrence of possible phase transitions in the family of $MeHSeO_3$, are of interest. The synthesis of the alkali hydrogen selenites, their crystal growth, and their study by nuclear magnetic resonance have recently been initiated at the Institute of Physics in Krasnoyarsk.

Prior to our work the crystal structure had been determined only for $NaHSeO_3$ crystals in 1963 by X-ray techniques (*1*). Data presented in this paper indicate that sodium hydrogen selenite crystallizes in the monoclinic system, space group C_{2h}^6, with 16 molecules in the unit cell, which contains two Na^+ ions and two hydrogen bonds with an O . . . O length of 2.75 and 2.90 Å. The hydrogen bonds are rather long in comparison with the values of 2.5–2.6 Å measured in the trihydrogen selenite crystals. In addition, dimeric $[Se_2O_4(OH)_2]^{2-}$ ions with an unexpected configuration undetected earlier in the compounds of selenious acid was reported to exist in the structure proposed by Chou *et al.* (*1*).

We investigated the single crystals of sodium deuterium selenite by deuteron magnetic resonance to determine the structural parameters for the hydrogen bonds and to compare them with those cited in Ref. (*1*). To obtain the information about local surrounding of the sodium ions we analyzed the ^{23}Na NMR spectra. Our experimental results are described in (*2*). The lengths of hydrogen bonds determined from our DMR data are 2.55 and 2.61 Å; these compare well with those reported for the trihydrogen

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selenites (*3*) and differ from those reported by Chou *et al.* The orientation of the q_{zz} components of the deuteron quadrupole coupling tensors with respect to the crystal axes does not coincide with the direction of the O . . . O bonds as calculated in (*1*). This leads to the conclusion that the structure reported by Chou, Hu and Yu is incorrect.

The disagreement between the DMR and X-ray data stimulated the reinvestigation by X-ray techniques of the $NaHSeO_3$ structure by Chomnilpan *et al.* (*4*). The results of this work coincide very well with the DMR data and confirm that data cited in Ref. (*1*) are incorrect. This paper presents the results of a joint analysis of the X-ray work by Chomnilpan *et al.* and of the present DMR investigation.

Experimental

Sodium deuterium selenite was prepared as described in (*5*) by the reaction

$$Na_2CO_3 + 2\ SeO_2 + 2\ D_2O = 2NaDSeO_3 + D_2O + CO_2.$$

The single crystals were grown by evaporation from saturated heavy water solution around 40°C. Three single-crystal specimens were prepared for the experiments.

Deuteron magnetic resonance spectra were recorded in a magnetic field about 13 kG as a function of the angle of rotation of rf probe about the axis perpendicular to the applied dc field. Angular dependences of the first-order quadrupole splittings of the spectra were measured for crystal rotation about three mutually orthogonal axes $X \| [b \times c]$ or a^*, $Y \| b$, $Z \| c$ (a, b, c correspond to (*1, 4*)). From the rotation patterns the principal values and the direction cosines of the electric field gradient (EFG) tensors, the values of the quadrupole coupling constant eQq/h, and the asymmetry parameters η were determined by the Volkoff method (*6*). The results are tabulated in Tables I and II.

TABLE I

PRINCIPAL VALUES AND DIRECTION COSINES OF THE PRINCIPAL AXES OF THE ^{2}D FIELD-GRADIENT TENSORS IN SODIUM HYDROGEN SELENITE

	eQq_{ii}/h (kHz)	Direction cosines with respect to *X*	*Y*	*Z*
D(1)	172.8	0.7923	±0.5288	−0.3040
	−92.5	∓0.6083	0.6473	∓0.4591
	−80.3	−0.0459	±0.5488	0.8346
D(2)	152.5	0.9750	±0.1882	0.1180
	−82.8	−0.1382	±0.0979	0.9855
	−69.7	∓0.1739	0.9772	∓0.1215

Results and Discussion

According to the specified data of Chomnilpan *et al.*, $NaHSeO_3$ is monoclinic, *C*2/*c*, a = 21.9799 Å, b = 5.7910 Å, c = 10.2796 Å, Z = 16. The asymmetric unit consists of two Na^+ ions with different environment and two $HSeO_3^-$ ions. The pyramidal $HSeO_3^-$ ions are bounded by hydrogen bonds O(2) . . . O(1) and O(4) . . . O(6) to form centrosymmetric dimers (Fig. 1). The indices 1–6 correspond to (*4*). Therefore, there will be two EFG tensors at hydrogen atoms.

At room temperature four pairs of DMR lines were observed with H_0 in an arbitrary direction and two pairs were observed with H_0 in a^*c plane. The rotation patterns of the DMR spectra about a^* and b axes are shown in Fig. 2. From the DMR data there are two nonequivalent sites D(1) and D(2) in the unit cell corresponding to two hydrogen bonds. The lengths of hydrogen bonds calculated from values of quadrupole coupling constants with empirical relation of Chiba (*7*) are given in Table II and compared with the X-ray data. Each field-gradient tensor was related to the specific hydrogen bond (Table II) by means of the

TABLE II

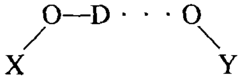
EXPERIMENTAL DATA[a]

	eQq/h (kHz)	η	R(O . . . O) Å X-ray (*4*)	R(O . . . O) Å DMR	φ_z	φ_y	Assignment
D(1)	172.8	0.07	2.656	2.61	2°	43°	O(6)–H · · · O(4)
						33°	O(4)–H · · · O(6)
D(2)	152.5	0.08	2.589	2.55	4°	9°	O(2)–H · · · O(1)
						56°	O(1)–H · · · O(2)

[a] Deuteron quadrupole coupling constants eQq/h, asymmetry parameters η, assignments of the field-gradient tensors to the hydrogen bond system, and hydrogen bond lengths of NaDSeO$_3$. Angles φ_z are between the q_{zz} directions and the assigned hydrogen bond O · · · O directions; angles φ_y are between the q_{yy} directions and the calculated directions perpendicular to the Se–O · · · O plane.

empirical relation (*7*) that the principal Z axis of the EFG tensor is nearly parallel to the hydrogen bond direction. D(1) lies on hydrogen bonds O(6) . . . O(4) and involves HSe(2)O$_3^-$; D(2) lies on hydrogen bonds O(2) . . . O(1) and involves HSe(1)O$_3^-$ (Fig. 1). The direction of the principal Z axis of the EFG tensor is close to the hydrogen bond direction; its deviation from the calculated O . . . O direction is 2° for D(1) and 4° for D(2). Therefore, the structure proposed by Chomnilpan *et al.* is in agreement with the DMR data.

The q_{yy} component of the EFG tensor characterizes the potential surface of the hydrogen bond. Experiments have shown (*7*) that in the



bonds the q_{yy} component of EFG tensor is normal to the X–O–D or X–O · · · O plane within about 10°. Thus, from the analysis of the φ_y angles between q_{yy} and the normal to the Se–O · · · O plane, one can determine which of the two oxygen atoms the hydrogen atom is attached to. When the hydrogen atom jumps back and forth between the equilibrium position of a double-minimum potential at a rapid rate (usually of the order of 10^5 Hz), the observed q_{yy} axis direction forms approximately the bisector of the angle between the two plane normals.

φ_y angles of NaDSeO$_3$ are given in Table II. For D(2) deuterons forming a hydrogen bonds O(1) · · · O(2), the direction of q_{yy} deviates by 9 and 56° from the normals to the Se(1)–O(2) · · · O(1) and Se(1)–O(1) · · · O(2) planes, respectively (see Fig. 1, Table II). Therefore, the deuterons D(2) are ordered in an asymmetric single-minimum potential near O(2). For D(1) deuterons forming a hydrogen bond O(6) · · · O(4) the observed direction of the q_{yy} axis deviates of 43 and 33° either from the direction perpendicular to the Se(2)–O(6) · · · O(4) plane or from the direction perpendicular to the Se(2)–O(4) · · · O(6) plane. Thus, the q_{yy} direction is close to the direction of the bisector of the angle between the two plane normals and this provides direct evidence for the fact that the deuterons D(1) jump

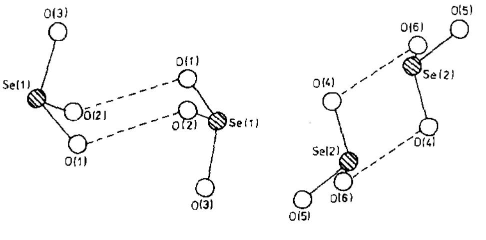


FIG. 1. The dimers [HSeO$_3^-$]$_2$ of NaHSeO$_3$ crystals projected on the (*ac*) plane. Dotted lines indicate hydrogen bonds.

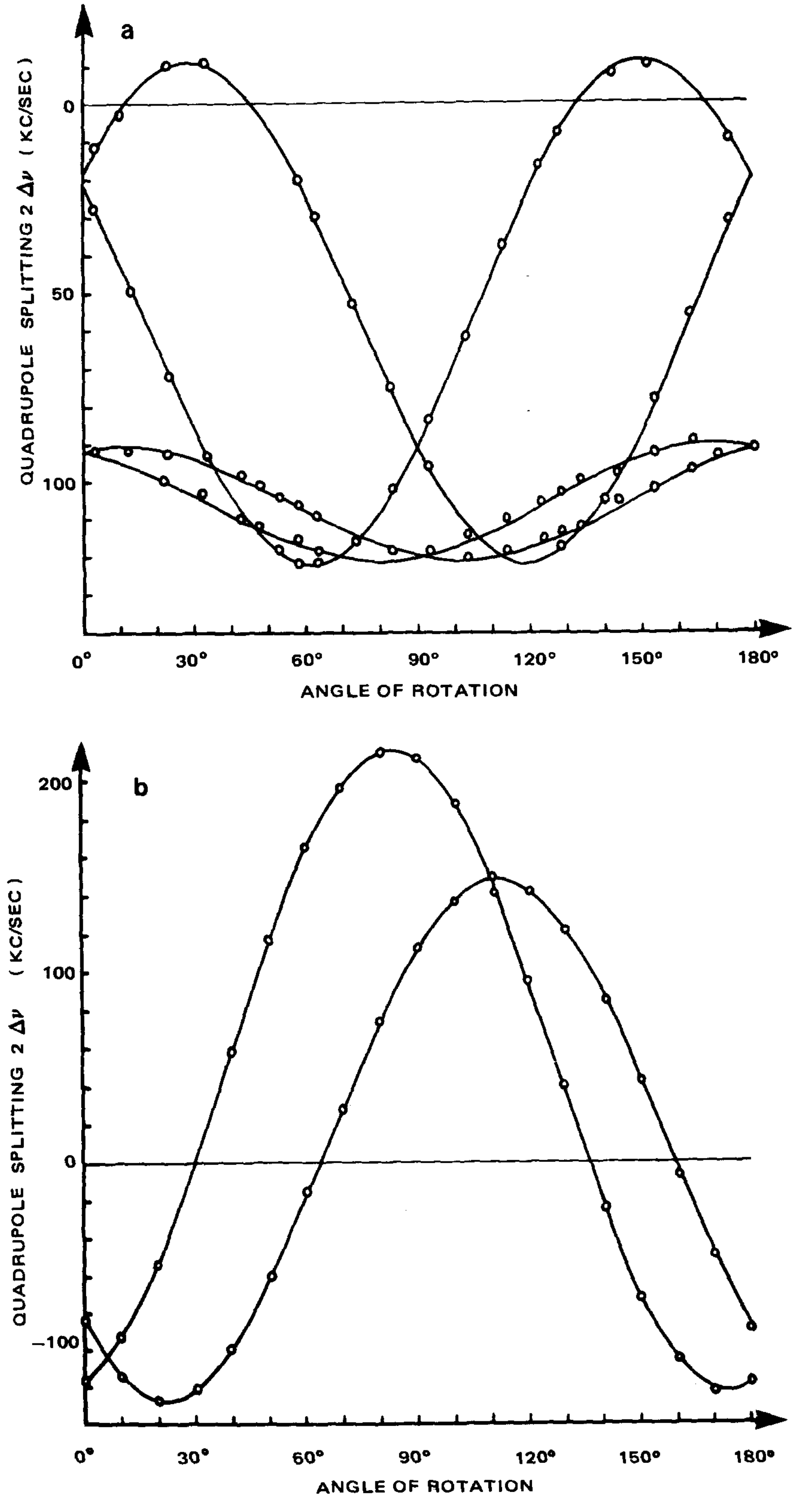


FIG. 2. Rotation patterns of the quadrupole splitting of DMR absorption lines of $NaDSeO_3$. (a) $H_0 \perp a^*$, $\theta = \sphericalangle b, H_0$; (b) $H_0 \perp b$, $\theta = \sphericalangle c, H_0$.

between the two sites of the double minima potential.

Some assumptions concerning the hydrogen atom positions have been reported by Chomnilpan *et al.* from the analysis of the Se–O distances in $NaHSeO_3$. Previous studies of the alkali-metal trihydrogen selenites have shown (*8*) that a pure Se–O bond is about 1.65 Å in length whereas an Se–OH bond is about 1.75 Å in length. For the case where H atoms are disordered in half-occupied positions, Se–O distances of about 1.70 Å have been observed. Based on this prior evidence Chomnilpan *et al.* assumed that the H atoms of $NaHSeO_3$ are ordered in Se(1) dimers, with Se(1)–O(2) corresponding to an Se–OH bond, but disordered for the others and distributed between O(4) and O(6), respectively (Fig. 2). These conclusions of X-ray data agree with the DMR results.

The disordered hydrogen bonds in the alkali-metal trihydrogen selenites had been discovered earlier (*8, 9*). At low temperatures the crystals of this family undergo a transition to an ordered state, with ferro- or antiferroelectric properties. Thus, a search of the phase transition in $NaHSeO_3$ crystals is of interest. Earlier we measured the temperature dependence of the ^{23}Na NMR spectra, to detect possible phase transitions; none was found in the temperature range 133 to 336 K (*2*). After the accurate structure of $NaHSeO_3$ with the disordered H atoms was published, we turned to a search of the phase transitions and measured the dielectric constant along *a*, *b*, and *c* directions up to 77 K. The dielectric constant is essentially independent of temperature for protonated and deuterated single crystals. Possibly, an ordered state is encountered below 77 K, but this is uncertain.

References

1. K. Chou, S. Hu, and D. Yu, *Sci. Sin.* **12**(12), 1938 (1963).
2. A. I. Roslyakov and I. S. Vinogradova, *Sov. Phys. Crystallogr.* **24**, 478 (1979).
3. S. Chomnilpan, R. Tellgren, and R. Liminga, *Acta Crystallogr. Sect. B* **34**, 373 (1978).
4. S. Chomnilpan, R. Liminga, E. J. Sonneveld, and J. W. Visser, *Acta Crystallogr. Sect. B* **37**, 2217 (1981).
5. L. F. Nilson, "Researches on the Salts of Selenious Acid." Uppsala: Berlig (1875).
6. G. M. Volkoff, H. E. Petch, and D. W. L. Smellie, *Canad. J. Phys.* **30**, 270 (1953).
7. G. Soda and T. Chiba, *J. Phys. Soc. Japan* **26**, 249 (1969).
8. S. Chomnilpan, R. Tellgren, and R. Liminga, *Acta Crystallogr. Sect. B* **34**, 373 (1978).
9. M. S. Lehman and F. K. Larsen, *Acta Chem. Scand.* **25**, 3859 (1971).