Deuteron and Proton Magnetic Resonance Studies of Potassium and Rubidium Hydrogen Selenite Single Crystals

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Deuteron and proton magnetic resonance studies of single crystals of potassium and rubidium deuterium (hydrogen) selenites are reported. Triclinic unit cells and structural isomorphism of both crystals are found. The deuterium field-gradient tensor is determined at room temperature. The quadrupole coupling constants (e^2Qq/h) are 172.9 kHz for $KDSeO_3$ and 181.6 kHz for $RbDSeO_3$. The observed field-gradient tensor corresponds to one nonequivalent hydrogen bond in the unit cell of length 2.60 Å in $KDSeO_3$ and 2.63 Å in $RbDSeO_3$. The deuterons are ordered; no phase transitions were found in the temperature range from room temperature to 77 K. The hydrogen atoms form chains running in the [100] direction and give rise to complicated proton magnetic resonance spectra (pair lines and others). A discussion of the crystal structures and physical properties of crystals of trihydrogen and hydrogen selenites is also presented. © 1986 Academic Press, Inc.

Introduction

This investigation is part of a series on the study of crystal structures and physical properties of alkali-metal hydrogen selenites $MHSeO_3$ (M = alkali metal). So far the crystal structures of $LiHSeO_3$ (*1*) and of $NaHSeO_3$ (*2*) have been determined by X-ray, and $KHSeO_3$, by neutron diffraction (ND) methods (*3*). The infrared and Raman spectra of $MHSeO_3$, with M = Li, Na, K, and Cs, have been studied; a low-temperature proton-triggered phase transition is observed in $CsHSeO_3$ and $KHSeO_3$ (*4*). Therefore, the study of crystal structures, especially of the hydrogen bond network, and of proton dynamic, as well as physical properties and possible phase transitions in the family $MHSeO_3$ are of interest.

We investigated single crystals of potassium and rubidium hydrogen selenites and their deuterated analogs by proton and deuteron magnetic resonance. The triclinic unit cells and isomorphism of these compounds have been established. The parameters of hydrogen bonds were determined and a comparison with the neutron diffraction study of $KHSeO_3$ was carried out. A search of a phase transition in a low-temperature region was also made.

Experimental

Potassium and rubidium deuterium selenites were prepared as described in (*5*) by the reaction

$$M_2CO_3 + SeO_2 + 2D_2O = 2MDSeO_3$$
$$+ D_2O + CO_2 \quad M = K, Rb$$
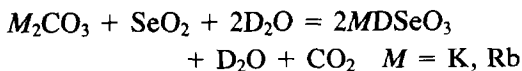
Protonated compounds were synthesized by the same reaction in H_2O. Single crystals were grown by evaporation from saturated

solutions close to room temperature. Crystal habits shown in Fig. 1a indicate the possible isomorphism of both crystals.

We began our work on the spectra NMR study without any data pertaining to point groups and unit cell parameters. To determine the ^{2}D field-gradient tensors of KDSeO$_3$ and RbDSeO$_3$ we chose three mutually orthogonal axes X, Y, Z that were based on the crystal habit (Fig. 1a). The crystals of KHSeO$_3$ and RbHSeO$_3$ possess a cleavage planes. Thus, the Z axis was chosen perpendicular to this cleavage plane, the X axis, perpendicular to the plane of Fig. 1a, and the Y axis, perpendicular to the X and Z axes. Recently, the crystal structure of KHSeO$_3$ was determined by neutron diffraction (3). Taking into account these data our crystal-fixed coordinate system was defined as follows. The X axis is parallel to the a-axis, the Z axis is perpendicular to the (001) plane (the cleavage plane), and the Y axis is situated in the (001) plane, perpendicular to the X and Z axes (Fig. 1b).

Proton and deuteron magnetic resonance spectra have been measured with a wideline NMR spectrometer in a magnetic field of roughly 10 and 13 kG, respectively. Measurements were made as a function of the

TABLE I

PRINCIPAL VALUES AND DIRECTION COSINES OF THE PRINCIPAL AXES OF THE ^{2}D FIELD-GRADIENT TENSORS IN KDSeO$_3$ AND RbDSeO$_3$

Single crystal	e^2Qq_{ii}/h (kHz)	Direction cosines with respect to		
		X	Y	Z
KDSeO$_3$	80.10	0.3028	0.8391	0.4518
	92.80	0.9405	−0.3397	0.0095
	−172.90	−0.1539	−0.4248	0.8921
RbDSeO$_3$	78.93	0.5289	0.7406	0.4144
	101.66	0.8366	−0.5370	−0.1081
	−181.60	−0.1425	−0.4039	0.9036

angle of rotation of the rf probe about the axis perpendicular to the applied dc field for every 10° of rotation of the crystal. Rotational data about the three mutually perpendicular axes (X, Y, Z) have been taken at room temperature. From the rotation patterns of the DMR spectra the principal values and the direction cosines of the electric field-gradient (EFG) tensors, the values of quadrupole coupling constant e^2Qq/h, and the asymmetry parameter η were determined by the Volkoff method (6). The results are tabulated in Tables I and II.

Results and Discussion

Deuteron magnetic resonance. To define the hydrogen bond parameters and deuteron position in hydrogen bonds (ordered or disordered) we studied the deuteron magnetic resonance spectra at room temperature.[1] One pair of DMR lines was observed for all angles of rotation of single crystals of KDSeO$_3$ and RbDSeO$_3$ relative to B_0, thus exhibiting the triclinic symmetry of both crystals. The rotation patterns of the quadrupole splitting of DMR spectra are given in Fig. 2. The most striking feature of this figure is the similarity in angular dependence of $2\Delta\nu$ in both crystals.
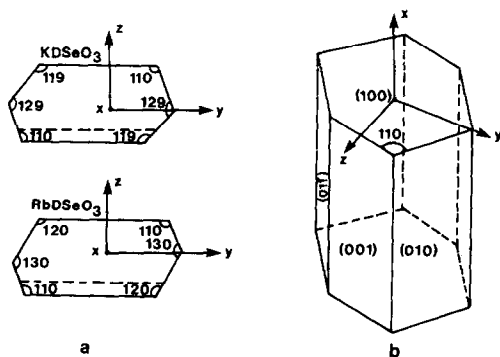

FIG. 1. Crystal habit and choice of axis system. (a) Arrangement in the plane situated perpendicular to the glide plane shown by dotted lines. (b) Typical crystal habit; the indexes of planes correspond to data of Ref. (3).

[1] Preliminary results of DMR spectra study on KDSeO$_3$ single crystal were reported in (7).

TABLE II

EXPERIMENTAL DATA[a]

Single crystal	e^2Qq/h (kHz)	η	$R(O \cdots O)$, Å		φ_z	φ_z^*	φ_y	Assignment
			ND[b]	DMR				
KDSeO$_3$	172.9	0.07	2.75	2.60	11°	0°	11°	Se–O(3) $\cdots$ O(2)
							74°	Se–O(2) $\cdots$ O(3)
RbDSeO$_3$	181.6	0.12	—	2.63				

[a] Deuteron quadrupole coupling constants e^2Qq/h, asymmetry parameters η and hydrogen bond lengths of KDSeO$_3$ and RbDSeO$_3$. Assignment of the EFG tensor to the hydrogen bond system of KHSeO$_3$ is given. Angles φ_z and φ_z^* are between the q_{zz} direction and the assigned hydrogen bond O $\cdots$ O and O–H directions, respectively. Angles φ_y are between the q_{yy} direction and the calculated directions perpendicular to the Se–O(2) $\cdots$ O(3) and Se–O(3) $\cdots$ O(2) planes.

[b] Bond distance for a protonated sample of KHSeO$_3$ (Ref. (3)).

Apparently, they are structurally equivalent.

There is one nonequivalent ^{2}D EFG tensor in the unit cell of each crystal corresponding to one hydrogen bond. The principal values and direction cosines of the EFG tensors of KDSeO$_3$ and RbDSeO$_3$ determined from the rotation patterns by the Volkoff method (6) are given in Table I. Using the relation between e^2Qq/h values and O $\cdots$ O distances developed by Chiba (8) we calculated the hydrogen bond
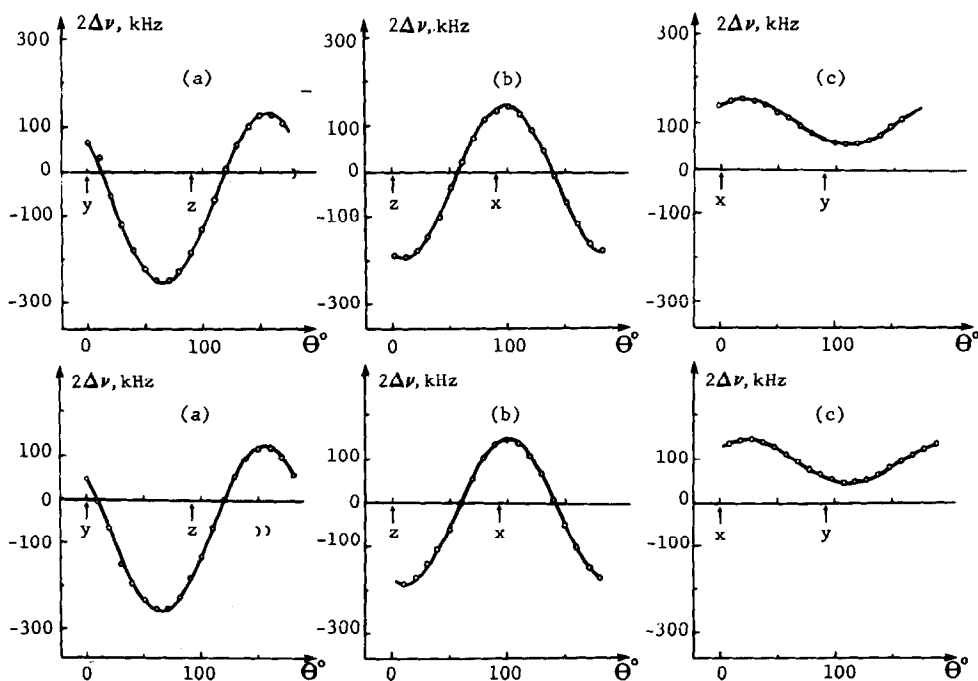

FIG. 2. Rotation patterns of the quadrupole splitting of DMR absorption lines of KHSeO$_3$ (top) and RbDSeO$_3$ (bottom). (a) $B_0 \perp X$, $\theta = \measuredangle B_0, Y$; (b) $B_0 \perp Y$, $\theta = \measuredangle B_0, Z$; (c) $B_0 \perp Z$, $\theta = \measuredangle B_0, X$.

lengths which are 2.60 Å in KDSeO$_3$ and 2.63 Å in RbDSeO$_3$. These compare well with those reported for trihydrogen selenites (9), for LiHSeO$_3$ (1), and for NaHSeO$_3$ (2).

Recently, a neutron diffraction study of KHSeO$_3$ was carried out (3). The triclinic symmetry of the crystals found earlier from the ESR spectra study of γ-irradiated KHSeO$_3$ single crystals (10) and from preliminary DMR spectra study of KDSeO$_3$ has been confirmed. The unit cell is found to be very small; it contains two formula units. The structure consists of HSeO$_3^-$ ions forming centrosymmetric dimers (Fig. 3). The HSeO$_3^-$ ion is pyramidal, with two shorter Se–O bonds (1.649 and 1.674 Å) and one longer Se–OH bond (1.784 Å), in agreement with similar bonds of HSeO$_3^-$ ions in the others selenites (9). The centrosymmetric space group $P\bar{1}$ assumed in the ND study was confirmed by the present DMR study. Two hydrogen bonds of the unit cell are equivalent for the centrosymmetric dimer; we therefore found only one ^{2}D EFG tensor.

There is a large discrepancy between the deuterium NMR and the ND values for the hydrogen bond length (Table II). The value of 2.75 Å (ND data in KHSeO$_3$) seems to be significantly longer than the corresponding values for MH$_3$(SeO$_3$)$_2$ crystals (2.52–2.65 Å) (9) as well as for NaHSeO$_3$ (2.65 and

2.59 Å) (2), LiHSeO$_3$ (2.62 Å) and also longer than the value of 2.60 Å determined from DMR data in KDSeO$_3$.

ND data have shown that hydrogen atoms of KHSeO$_3$ are ordered in a single asymmetric minimum potential well. The independent method of proton localization is the DMR method. The analysis of the DMR data has been developed by Chiba (8). He has shown that the direction of the principal Z axis of the EFG tensor is close to the hydrogen bond direction. We have calculated that in KHSeO$_3$ crystals the deviation of q_{zz} from the O(3) $\cdots$ O(2) and O(3)–H directions are 11° and 0°, respectively. Therefore, the structure based on ND data is in agreement with DMR data. The q_{yy} component of the EFG tensor characterizes the potential surface of the hydrogen bond. Experiments have shown (8) that in the bonds in

$$O\!-\!D \cdots O$$

with X on the left below and Y on the right below.
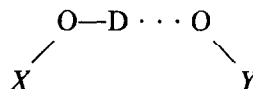
the q_{yy} component of the EFG tensor is normal to the X–O–D or X–O $\cdots$ O plane within about 10°. From the analysis of the angles between q_{yy} and the normal to the Se–O $\cdots$ O plane, one can determine which of the two oxygen atoms has the hydrogen atom attached to it. The φ_y angles of KDSeO$_3$ are given in Table II. The direction of q_{yy} deviates by 11° and 74° from the normals to the Se–O(3) $\cdots$ O(2) and Se–O(2) $\cdots$ O(3) planes, respectively. Therefore, the deuterons are ordered in an asymmetric single-minimum potential well near O(3). The same result follows from the ND study. Thus, our DMR data confirm the hydrogen bond network of KHSeO$_3$ based on ND.

Proton magnetic resonance. The proton system of KHSeO$_3$ and RbHSeO$_3$ crystals essentially differs from that of the trihydrogen selenites as is seen from the spectra of proton magnetic resonance. The PMR
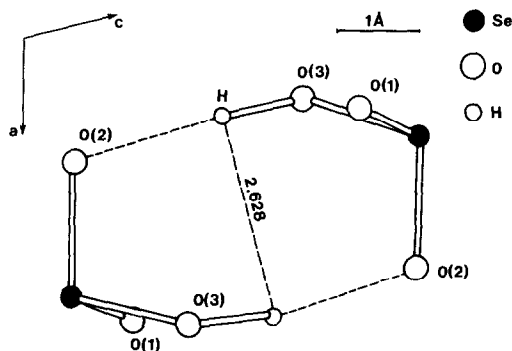

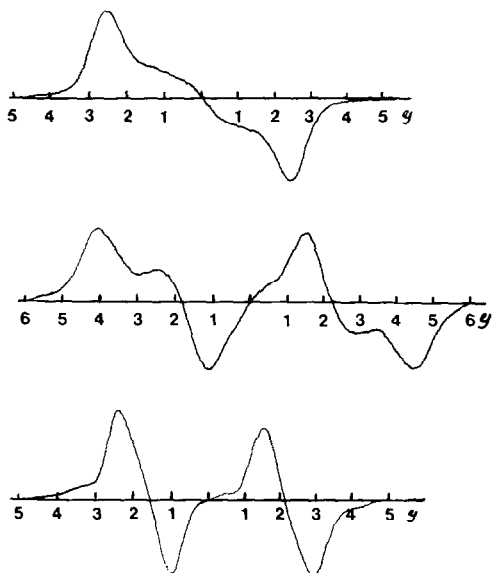FIG. 3. Dimer (HSeO$_3^-$)$_2$ of KHSeO$_3$ crystal structure from data of Ref. (3).

FIG. 4. PMR spectra in several orientations for a crystal of $KHSeO_3$ relative to B_0 in XY plane ($B_0 \perp Z$).

spectra of trihydrogen selenites typically consist of single lines. In crystals of hydrogen selenites of potassium and rubidium we encountered rather complex spectra, which depended strongly on the orientation of crystals relative to magnetic field B_0. In many orientations well-split pair lines are observed (Fig. 4). In the separate dimers $(HSeO_3^-)_2$ of $KHSeO_3$ crystal the protons form isolated pairs with a proton–proton distance of 2.63 Å (3) (Fig. 3). The PMR spectra of such system must yield paired lines with a Pake dependence of the splitting. However, such a dependence of the splitting is not observed experimentally; this is connected with the fact that in the bulk of the crystal chains of protons run along the crystallographic a-axis. The H–H distances within the dimer (2.628 Å) and between dimers (2.798 Å) are very similar. such chains of protons produce the complicated PMR spectra. We recorded the PMR spectra of $KHSeO_3$ and $RbHSeO_3$ single crystals for crystal rotations about X, Y, Z axes. The spectra are very similar in both

crystals. This fact confirms their isomorphism and the presence of the $(HSeO_3^-)_2$ dimers as well as the chains of protons in $RbHSeO_3$ crystals.

A low crystal symmetry, a small unit cell, and a special proton configuration make $KHSeO_3$ and $RbHSeO_3$ crystals convenient objects for the calculation of the PMR spectra; such work is in progress.

The search of phase transition in $KHSeO_3$. Two points are noteworthy in the phase transition in $KHSeO_3$. Vedam and Pepinsky in 1959 (11) optically observed a phase transition at $-39°C$; however, no dielectric anomaly could be detected at this temperature. The second report of possible phase transition was published in 1978 (4). Cody et al. investigated the infrared and Raman spectra of polycrystalline alkali hydrogen selenites $MHSeO_3$ (M = Li, Na, K, Cs) and their deuterated analogs. The spectra of $KHSeO_3$ and $CsHSeO_3$ at 77 K differed from the room-temperature spectra. It was inferred from these data that a phase transition had taken place. But since the spectra were recorded only at two temperatures and the temperature of the phase transition was not determined this interpretation is quite tentative.

It was of great interest for us to confirm the possible presence of a phase transition by other methods. Earlier we investigated the ESR spectra of γ-irradiated single crystals of $KHSeO_3$ and $RbHSeO_3$; also, the parameters of the g-tensor and the selenium hyperfine tensor have been determined at room temperature (10). We have found that stable SeO_2^- radicals are formed as in the case of trihydrogen selenite crystals. The ESR spectra of SeO_2^- radicals are very sensitive to the occurrence of phase transitions (12) in trihydrogen selenite crystals. Therefore we measured the angular dependences of the ESR spectra of $KHSeO_3$ and $KDSeO_3$ at room temperature and at $-150°C$. We have not encountered any changes in spectra that would indicate a phase transi-

tion. Our results so disagree with (4) and (11) data.

There is the disagreement between vibrational spectra data (4) on the one hand and the ND and DMR data on the other hand concerning the proton position in the hydrogen bonds of the KHSeO$_3$ crystal lattice. It was inferred from observation of Raman spectra of polycrystalline KHSeO$_3$ and CsHSeO$_3$ that spectra are characteristic of SeO$_2^-$ units; therefore, K$^+$ and Cs$^+$ salts contain disordered protons at room temperature. At liquid-nitrogen temperature the spectra indicate the presence of HSeO$_3^-$ ions, showing that a phase transition is connected with the ordering of the protons. The neutron diffraction study of KHSeO$_3$ and the present DMR study of KDSeO$_3$ single crystals have shown that protons are already ordered at room temperature.

There is a discrepancy between the conclusions of Ref. (4) and the diffraction data for NaHSeO$_3$. According to (4) the protons in NaHSeO$_3$ are ordered at room temperature. However, in the paper (13) devoted to the X-ray study of NaHSeO$_3$, from the analysis of Se–O distances it was inferred that protons are ordered on one of the hydrogen bonds of the unit cell and disordered on the other. This supposition was confirmed by the DMR data for NaDSeO$_3$ (14) and the recent neutron diffraction study of NaHSeO$_3$ and NaDSeO$_3$ single crystals (15).

Thus, the conclusions of (4) on hydrogen bonds and protons dynamics are not confirmed by the diffraction and DMR data as far as with respect to the occurrence of phase transitions in KHSeO$_3$ and CsHSeO$_3$ (we have studied CsHSeO$_3$ and CsDSeO$_3$ single crystals by ^{133}Cs NMR from room temperature up to −140°C and have not found a phase transition, unpublished data).

The presence of phase transition in KHSeO$_3$ has also been checked by other methods. We have measured a dielectric constant along X, Y, and Z directions; it essentially remains unchanged at all temperatures to liquid-nitrogen temperature; such a peculiarity is typical of all MHSeO$_3$ single crystals. We have studied thin single crystal plates under polarized light in a microscope, KR spectra of polycrystalline KHSeO$_3$ and, finally, ^{77}Se NMR spectra, all with the aim of searching for a phase transition, without success. Apparently, the results published in (4) and (10) are erroneous; it is thus necessary to carry out a careful reinvestigation of the Raman spectra of KHSeO$_3$ and of the other MHSeO$_3$ salts. In RbHSeO$_3$ single crystals we have searched for a phase transition using dielectric constant and ^{77}Se NMR measurements. The results are the same as for KHSeO$_3$.

Comparison of some properties of hydrogen and trihydrogen selenites. At present, the crystal structures of hydrogen selenites of lithium, sodium, and potassium are determined and there exist NMR data for RbHSeO$_3$. It is of interest to discuss these structures and to compare them with those of the trihydrogen selenites. The unit cells of the crystals of both families consist of alkali ions and of pyramidal SeO$_3$ groups interlinked by hydrogen bonds. The structural parameters of SeO$_3$ groups are similar in the crystals of both families and depend on the proton position in the hydrogen bonds. Thus, a pure Se–O bond is about 1.65 Å in length whereas a Se–OH bond is about 1.75 Å. For the disordered case the Se–O bond length is approximately 1.70 Å.

There are some typical peculiarities in structures and properties of hydrogen selenites MHSeO$_3$. The first is the existence of hydrogen-bonded centrosymmetric dimers (HSeO$_3^-$)$_2$. Such dimers are found in the Na$^+$, K$^+$, and Rb$^+$ salts. For the present the exception is the LiHSeO$_3$ crystal structure which consists of hydrogen-bonded HSeO$_3^-$ ions that form spiral chains. In this sense LiHSeO$_3$ is similar to the trihydrogen

selenite crystals, the unit cells of which contain hydrogen-bonded chains of $HSeO_3^-$ ions and H_2SeO_3 molecules. Thus, the proton configurations of hydrogen selenites of sodium, potassium, and rubidium differ considerably from those of corresponding salts of trihydrogen selenites. Apparently, in the family of $MHSeO_3$ as in the case of $MH_3(SeO_3)_2$ the proton system to a certain extent defines the properties of crystals.

The second peculiarity of hydrogen selenites in comparison with trihydrogen selenites is the rigidity of their unit cells which do not undergo a phase transition in the low-temperature region. We have studied the temperature dependences of the quadrupole splitting of alkali-ion spectra: ^{23}Na in $NaHSeO_3$ (16), ^7Li in $LiHSeO_3$, and ^{133}Cs in $CsHSeO_3$ (unpublished data) as well as the ^{77}Se NMR in $KHSeO_3$ and $RbHSeO_3$ (to be published) with the aim of detecting a phase transitions. Neither the spectral form nor the angular dependences change appreciably over a wide temperature range. Even the presence of proton disorder found in $NaHSeO_3$ (2, 14, 15) at room temperature does not lead to a transition to an ordered phase up to 77 K. At the same time trihydrogen selenite crystals undergo a structural phase transitions in the low-temperature region. These transitions are followed by the ordering of hydrogen atoms, which are disordered in two minima potential well at room temperature.

The study of other physical properties of hydrogen selenites and comparison with those of trihydrogen selenites also are of interest.

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