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Nuclear quadrupole double resonance in AHSO$_4$ (A $\equiv$ K, Rb, Cs, Tl, NH$_4$)

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Abstract. Nuclear quadrupole resonance (NQR) spectra of ^{17}O, ^{39}K, ^{85}Rb, ^{87}Rb and ^{133}Cs have been measured in the low-temperature phases of KHSO$_4$, RbHSO$_4$, NH$_4$HSO$_4$ and TlHSO$_4$ with the nuclear quadrupole double-resonance technique based on magnetic field cycling. The NQR results are related to the crystal structures of the low-temperature phases of these compounds.

1. Introduction

H-bonded crystals of the AHSO$_4$ family (A $\equiv$ K, Rb, Cs, Tl, NH$_4$) exhibit a number of interesting physical properties. They undergo several structural phase transitions of different kinds. Two of these crystals, RbHSO$_4$ and NH$_4$HSO$_4$, are well known ferroelectrics. At elevated temperatures, AHSO$_4$ compounds are characterized by a high protonic ionic conductivity. The nature of the structural changes leading to superionic protonic mobilities is at present the subject of intensive studies. In order to understand the underlying physical mechanisms of superionic protonic conductivity we have to know the structure of the low-temperature phase, which is usually ordered, as well as the structure of the high-temperature superionic phase, which is usually disordered. This paper is devoted to the study of the local structure of the H-bond network and other structural characteristics of the low-temperature phase of a number of AHSO$_4$ compounds.

2. Theory

The local crystal structure of AHSO$_4$ compounds and the structural changes at the various phase transitions in these systems can be very well studied using nuclear quadrupole resonance (NQR) methods. The NQR technique is sometimes capable of detecting small nuclear displacements which are hard to observe with x-ray or neutron scattering as here— in contrast with NQR—the space- and time-averaged structure is measured. The NQR spectra differ for different nuclear spins I. In the case of $I = \frac{3}{2}$ (i.e. for Na, K and ^{87}Rb) there is only one pure NQR frequency at

$$\nu_Q = (eQV_{ZZ}/2h)\sqrt{1 + \eta^2/3}. \tag{1}$$

Here V_{ZZ} is the largest principal value of the traceless electric field gradient (EFG) tensor **V** at the nuclear site, $V_{ij} = \partial^2 V/(\partial x_i \partial x_j)$, eQ is the nuclear quadrupole moment, and the asymmetry parameter η is defined by

$$\eta = (V_{XX} - V_{YY})/V_{ZZ}. \tag{2}$$

The energy levels E for $I = \frac{5}{2}$ (^{85}Rb and ^{17}O) nuclei are obtained from the secular equation

$$x^3 - 7(3 + \eta^2)x - 20(1 - \eta^2) = 0 \tag{3}$$

where $E = xeQV_{ZZ}/20$. Here there are three NQR frequencies, and both the quadrupole coupling constant eQV_{ZZ} and the asymmetry parameter η can be determined separately. η is usually obtained from the frequency ratio $\nu_{1/2-3/2}/\nu_{3/2-5/2}$.

For nuclei with $I = \frac{7}{2}$ (^{133}Cs) the four NQR energy levels are calculated from

$$x^4 - 126x^2(3 + \eta^2) - 1728(1 - \eta^2) + 945(\eta^2 + 3)^2 = 0 \tag{4}$$

where $E = xeQV_{ZZ}/84$. The asymmetry parameter is obtained in a similar way as for the $I = \frac{5}{2}$ case.

The EFG tensor at the site of a nucleus depends on the electric charge distribution around the site and thus on the crystal structure. Nuclei of the same type lying on crystallographically inequivalent sites see different EFGs and have in general different NQR frequencies. NQR is thus a sensitive technique for the determination of the number of crystallographically inequivalent sites of a given atom in the unit cell.

Nuclei lying on crystallographically equivalent sites related by a symmetry operation have the same NQR frequencies. The EFG tensors at these sites have the same principal values whereas they differ in the orientations of their principal axes. On the application of an external magnetic field also the number of the symmetry-related sites of a given atom in the unit cell can be determined.

The form of the EFG tensor **V** depends also on the point symmetry at the site of the nucleus. Thus, for example, one principal axis of the EFG tensor is perpendicular to the mirror plane or parallel to the twofold axis going through the nuclear site. When the site of the nucleus is lying on a threefold or on a higher-symmetry axis, the EFG tensor is axially symmetric ($\eta = 0$) with the Z axis along the symmetry axis. Any displacement from this axis will produce a non-zero η.

In double-minimum-type O–H—O hydrogen bonds the ^{17}O NQR lines from the 'hydrogen-close' ^{17}O–H—O sites, i.e. sites to which the hydrogen is directly bonded, are broad and structured while the ^{17}O NQR lines from the 'hydrogen-far' O–H—^{17}O sites are narrow. This is a consequence of the usually unresolved ^{1}H–^{17}O magnetic dipolar interaction. From the widths and the structures of the ^{17}O NQR lines the oxygen–hydrogen distance and the orientation of the O–H bond in the principal frame of the EFG tensor at the oxygen site can be deduced [1, 2].

3. Experimental details

The nuclei of the alkali atoms and ^{17}O have in general low NQR frequencies of the order of 1 MHz, resulting in a poor signal-to-noise ratio of the NQR spectra. ^{17}O is in addition a rare nucleus with a natural abundance of 0.037%. This is the reason why we decided to measure the NQR frequencies with the help of nuclear quadrupole double resonance [3–5]. In this technique the proton system is first polarized in a high static magnetic field B_0. Then the static magnetic field is adiabatically reduced to zero. The proton system is now found in a metastable state characterized by a low spin temperature. The decay time $T_1(0)$ of the metastable state is called the spin–lattice relaxation time in zero magnetic field. After a time τ ($\tau \leqslant T_1(0)$), the magnetic field is adiabatically increased to the initial value B_0 and

the remaining proton magnetization is measured. It is reduced from the initial value M_0 at the beginning of the adiabatic demagnetization by a factor $exp[-\tau/T_1(0)]$.

When during the stay in zero static magnetic field an RF magnetic field is applied with a frequency close to the NQR frequency of an alkali atom or ^{17}O, the decay time of the protonic metastable state decreases and the remaining proton magnetization at the end of the magnetic field cycle drops to a lower value because of cross relaxation. Various nuclear quadrupole double-resonance techniques differ in the RF irradiation procedure in zero magnetic field.

In this work the ^{17}O, ^{39}K, ^{85}Rb and ^{87}Rb NQR frequencies have been determined with 180°-phase-modulated RF irradiation in zero magnetic field [6]. The modulation frequency was 300 Hz in the case of abundant nuclei and 1.5 kHz in the case of ^{17}O. The rubidium and potassium NQR frequencies were determined more precisely using the solid effect [7]. The structures of the ^{17}O NQR lines in TlHSO₄ were determined with two RF magnetic fields of different frequencies applied at the same time to a given NQR transition [1, 2]. The ^{133}Cs NQR frequencies were determined with the level-crossing technique [4].

4. Results and discussion

4.1. KHSO₄

The ^{39}K and ^{17}O NQR frequencies for KHSO₄ have been measured at 150 K. Two ^{39}K NQR lines have been observed at 740 ± 5 kHz and at 770 ± 5 kHz. Since ^{39}K has a spin $\frac{3}{2}$ and thus a single NQR transition, the two NQR frequencies correspond to two crystallographically inequivalent potassium sites in agreement with the crystal structure [8].

^{17}O has a spin $\frac{5}{2}$ and thus three NQR transitions with the frequencies $\nu_{1/2-3/2} \leqslant \nu_{3/2-5/2} < \nu_{1/2-5/2} = \nu_{1/2-3/2} + \nu_{3/2-5/2}$. In the ^{17}O NQR spectra of KHSO₄, two sets of three broad NQR lines corresponding to two inequivalent 'hydrogen-close' ^{17}O–H sites have been observed. The corresponding ^{17}O NQR frequencies, quadrupole coupling constants and asymmetry parameters are given in table 1. In addition, three narrow lines have been observed at 1140, 1210 and 2170 kHz corresponding to 'hydrogen-far' ^{17}O—H sites. This demonstrates that the O–H—O bonds in KHSO₄ are asymmetric. The two low-frequency lines correspond to two different $\frac{1}{2}-\frac{3}{2}$ transitions from two inequivalent 'hydrogen-far' ^{17}O—H sites while it is not clear to which of these ^{17}O nuclei one should assign the weak line at 2170 kHz. Part of the double-resonance spectra with the four $\frac{1}{2}-\frac{3}{2}$ transitions is shown in figure 1.

The presence of two inequivalent O–H sites and of two inequivalent O—H sites agrees with the crystal structure [8] of KHSO₄ which contains two asymmetric O–H—O hydrogen bonds of different lengths. It should be noted that the double-resonance signals from the non-hydrogen-bonded oxygen sites are generally rather weak and have not been observed.

As seen from figure 1 the ^{17}O—H NQR line at 1140 kHz is significantly weaker than the ^{17}O—H line at 1210 kHz. Similarly also the ^{17}O—H NQR line at 1930 kHz is somewhat weaker than the ^{17}O–H line at 1800 kHz. According to the crystal structure, half of the sulphate ions form cyclic dimers and the remainder form chains, with O–H—O bond lengths of about 2.67 Å. Thus the NQR lines should be of equal intensities. The fact that they are not suggests that the weaker lines are doublets. The differences in intensities are less pronounced at the ^{17}O–H sites. Here the NQR lines are broad and still overlap in a broad frequency region. On the other hand the ^{17}O—H NQR lines are narrow and the two lines of a doublet may not overlap. In this case a lower intensity is expected. Thus, according to the NQR data, not two but three types of O–H—O hydrogen bond are present in the structure. From the present NQR data it is not clear whether there are two types of slightly inequivalent O–H—O hydrogen bonds in a cyclic dimer or in a polymeric chain.
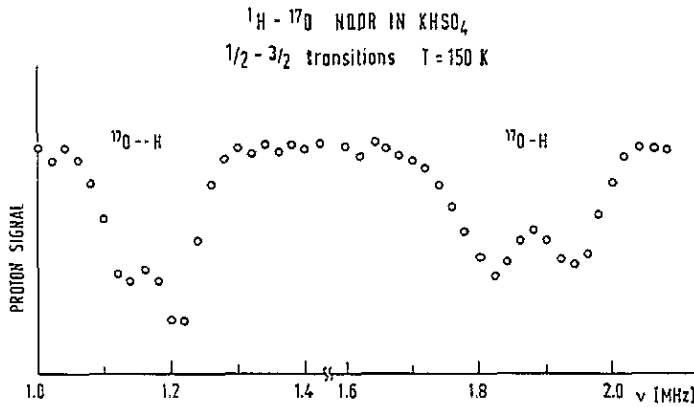
Figure 1. Double-resonance spectra of the $\frac{1}{2}-\frac{3}{2}$ ^{17}O NQR transitions for KHSO$_4$ at 150 K. The two narrow lines at 1140 and 1210 kHz correspond to the 'hydrogen-far' O—H sites, while the two broad lines at 1800 and 1930 kHz correspond to the 'hydrogen-close' O—H sites.

Table 1. ^{17}O NQR frequencies, quadrupole coupling constants and asymmetry parameters in AHSO$_4$ systems (A $\equiv$ K, NH$_4$, Tl).

A	T (K)	Site	$\nu_{1/2-3/2}$ (kHz)	$\nu_{3/2-5/2}$ (kHz)	$\lvert eQV_{zz}/h \rvert$ (kHz)	η
K	150	O–H	1800	2350	8440	0.69
		O–H	1930	2300	8410	0.79
		O—H	1140	—	—	—
		O—H	1210	—	—	—
NH$_4$	170	O–H	1780	2400	8570	0.65
		O–H	2000	2270	8370	0.85
		O—H	1110	—	—	—
		O—H	1150	—	—	—
Tl	163	O–H	1737	2349	+8379	0.650
		O—H	1115	2225	7420	0.04

The cyclic dimers could be dynamically disordered at higher temperatures [9]. Thus the temperature coefficients of the ^{17}O NQR frequencies from the dimers should be significantly different from the temperature coefficients of the ^{17}O NQR lines from the chains. The measurements performed at room temperature show that the ^{17}O NQR absorption frequencies within the set of frequencies at about 1200 kHz and within the set of frequencies at about 1900 kHz shift from the respective sets at $-150\,°C$ by nearly the same amount (about 30 kHz).

Thus the dynamical disorder of the cyclic dimers—if present—is weak. This may suggest that the two O–H—O hydrogen bonds in a dimer are slightly inequivalent.

Our results differ from the double-resonance data in [10] and [11] for KHSO$_4$ at room temperature which showed only a single potassium site with $\nu_Q = 715$ kHz and a single O–H—O hydrogen bond ($eQV_{ZZ(O-H)}/h = 8.38$ MHz; $\eta = 0.69$).

4.2. RbHSO$_4$

For RbHSO$_4$ the NQR measurements have been performed in the ferroelectric phase at

150 K. ^{85}Rb has a spin $\frac{5}{2}$ and, like ^{17}O, three NQR transitions. Its natural abundance is approximately $\frac{3}{4}$. ^{87}Rb has a spin $\frac{3}{2}$ and a single NQR transition. The magnetic moment of an ^{87}Rb nucleus is larger than the magnetic moment of an ^{85}Rb nucleus. The double-resonance signal of ^{87}Rb is generally stronger than the double-resonance signal of ^{85}Rb. The ratio $eQ(85)/eQ(87)$ of the two nuclear quadrupole moments is 2.063 [12].

In the double-resonance spectra of RbHSO$_4$, 12 low-frequency rubidium NQR lines have been observed in the ferroelectric phase at 150 K. Four of them at 1425, 1920, 2670 and 3770 kHz are stronger and broader than the other eight. They correspond to four inequivalent ^{87}Rb sites. The other eight double-resonance lines correspond to the four $\frac{1}{2}-\frac{3}{2}$ transitions and to the four $\frac{3}{2}-\frac{5}{2}$ transitions of four inequivalent ^{85}Rb nuclei. The ^{85}Rb NQR frequencies together with the Rb quadrupole constants and the asymmetry parameters are given in table 2.

Table 2. ^{85}Rb NQR frequencies, quadrupole coupling constants and asymmetry parameters in ferroelectric RbHSO$_4$ at 150 K.

$\nu_{1/2-3/2}$ (kHz)	$\nu_{3/2-5/2}$ (kHz)	eQV_{ZZ}/h (kHz)	η
1155	1530	5480	0.67
1320	2270	7750	0.37
2310	2740	· 10020	0.80
2840	4245	14870	0.53

The ^{17}O NQR lines have not been observed in the double-resonance spectra of RbHSO$_4$, since they are hidden within the much stronger rubidium lines.

According to the crystal structure [13] of paraelectric RbHSO$_4$, determined at 23 °C, there are two inequivalent rubidium sites and two inequivalent asymmetric O–H—O hydrogen bonds in the structure. Our data show that on going to the ferroelectric phase the number of inequivalent rubidium sites doubles. This agrees with the reduction in the symmetry on going from the paraelectric phase with the space group $P2_1/C$ to the ferroelectric phase with the space group Pc with the polar axis parallel to the C axis.

4.3. NH$_4$HSO$_4$

^{17}O NQR measurements for NH$_4$HSO$_4$ have been performed at 170 K, i.e. above the low-temperature phase transition. The ^{17}O NQR data are presented in table 1. Two sets of three broad ^{17}O NQR lines have been observed at frequencies close to the ^{17}O NQR frequencies observed for KHSO$_4$ and for H$_2$SO$_4$ [10]. From the O—H sites, only the two low-frequency $\frac{1}{2}-\frac{3}{2}$ transitions have been observed at 1110 and 1150 kHz. The NQR data show that there are two inequivalent asymmetric O–H—O hydrogen bonds in the ferroelectric phase, as in the paraelectric phase [14].

4.4. CsHSO$_4$

The measurements for CsHSO$_4$ have been performed at 150 K. Strong level-crossing signals from the ^{133}Cs nuclei have been observed at 28, 37, 42, 65, 70 and 107 kHz.

^{133}Cs has a spin $\frac{7}{2}$ and thus four nuclear quadrupole energy levels. None of the six transitions is forbidden when $\eta \neq 0$. Our NQR data show the presence of a single caesium site with a quadrupole coupling constant of 214 ± 2 kHz and with an asymmetry parameter $\eta = 0.87 \pm 0.02$.

The NQR data agree with the x-ray data [14] which show that the crystal structure of $CsHSO_4$ is not isomorphous with the crystal structures of non-ferroelectric $NaHSO_4$ and $KHSO_4$ or ferroelectric $RbHSO_4$ and NH_4HSO_4. For $CsHSO_4$ all caesium sites are crystallographically equivalent and the sulphate groups are linked by O–H—O hydrogen bonds of equal lengths. The hydrogen bonds seem to be disordered at room temperature [15].

4.5. $TlHSO_4$

The double-resonance measurements for $TlHSO_4$ have been performed at 163 K using a slightly enriched sample with a ^{17}O concentration of 0.5%. Three broad ^{17}O NQR lines have been observed at 1737, 2349 and 4086 kHz. Two additional narrow lines have been observed at 1115 and 2225 kHz.

The proton–^{17}O dipolar structures of the three broad ^{17}O NQR lines coming from the 'hydrogen-close' O–H sites are shown in figure 2. The analysis of the dipolar structures gives the O–H distance as 0.101 ± 0.001 nm. The O–H bond lies in the X–Z plane of the principal coordinate system of the ^{17}O EFG tensor forming an angle of $57° \pm 5°$ with the Z axis.
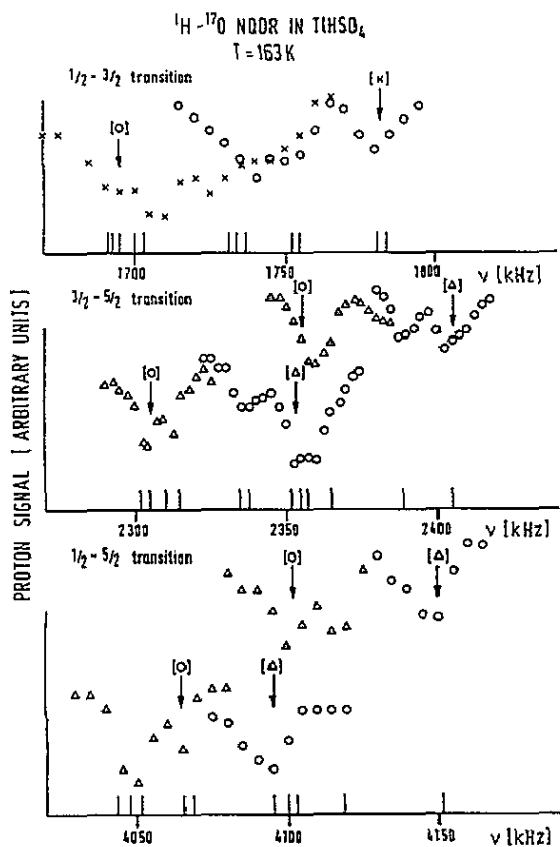

Figure 2. The dipolar structures of the three ^{17}O NQR lines for $TlHSO_4$ at 160 K obtained by two-frequency irradiation. The fixed frequencies are indicated by arrows. The positions of the individual dipolar lines calculated with the parameters given in the text are indicated as short vertical lines on the frequency scales.

The ^{17}O NQR data show the presence of a single asymmetric O–H—O hydrogen bond in the unit cell. Thus the crystal structure of $TlHSO_4$ is not isomorphous either with $NaHSO_4$ and $KHSO_4$ or with $RbHSO_4$ and NH_4HSO_4 but may be isomorphous with $CsHSO_4$.

5. Assignation of the ^{17}O—H spectra of AHSO$_4$ compounds

As far as the ^{17}O NQR data from the covalently bonded 'hydrogen-close' ^{17}O–H sites in the above compounds are concerned there is no doubt about the assignation of the NQR lines since, in these cases, sets of three NQR lines have been clearly observed.

The situation is less clear for the hydrogen-bonded O—H sites in the above compounds since at least one line of a set is always missing. That is, there is an overlap of the ^{17}O NQR lines from the O–H sites and from the O—H sites at around 2.3 MHz.

One possible interpretation of the ^{17}O—H NQR data is that the $\frac{1}{2}-\frac{3}{2}$ transition frequencies are at about 1100 kHz and the $\frac{3}{2}-\frac{5}{2}$ transition frequencies are at about 2200 kHz, giving an asymmetry parameter $\eta \simeq 0$ and a quadrupole coupling constant of about 7 MHz.

Another possible interpretation of the ^{17}O—H NQR data is that both the $\frac{1}{2}-\frac{3}{2}$ transition frequencies and the $\frac{3}{2}-\frac{5}{2}$ transition frequencies are at about 1100 kHz and the $\frac{1}{2}-\frac{5}{2}$ transition frequencies are at about 2200 kHz. In this case, $\eta \simeq 1$ and the quadrupole coupling constant is approximately 4 MHz.

Neither of the above two interpretations can be definitely excluded on the basis of the present ^{17}O NQR data. We have adopted the same interpretation as in [10] with $\eta \simeq 0$.

Further experiments in systems with short S–O–H—O=S hydrogen bonds are needed in order to clarify the situation.

6. Conclusions

From the above data the following conclusions can be made.

(1) The NQR double-resonance data for KHSO$_4$ clearly show the presence of two crystallographically inequivalent potassium sites and of two or three different asymmetric O–H—O hydrogen bonds in the unit cell. This agrees with the x-ray structure but disagrees with previous NQR studies.

(2) For RbHSO$_4$, four inequivalent rubidium sites have been observed in the ferroelectric phase, twice as many as in the paraelectric phase, in agreement with the proposed change in the crystal structure at the phase transition.

(3) For NH$_4$HSO$_4$, two inequivalent asymmetric O–H—O hydrogen bonds have been observed using NQR in the ferroelectric phase, as in the paraelectric phase by x-ray and neutron diffraction.

(4) For CsHSO$_4$ a single caesium site has been observed at 150 K. This agrees with the structural data which show that the crystal structure of CsHSO$_4$ differs from the crystal structures of NaHSO$_4$, KHSO$_4$, RbHSO$_4$ and NH$_4$HSO$_4$.

(5) For TlHSO$_4$ a single asymmetric O–H—O hydrogen bond has been observed at 163 K, suggesting that TlHSO$_4$ may be isostructural with CsHSO$_4$ but not with other members of this family.

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