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^{39}K nuclear magnetic resonance in a KHSO_4 single crystal

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Abstract

The ^{39}K NMR in a KHSO_4 single crystal grown by the slow evaporation method was investigated by employing a Bruker FT NMR spectrometer, and the ^{39}K quadrupole coupling was determined from the angular dependences of the four $^{39}\text{K} \pm 1/2 \leftrightarrow \mp 1/2$ central NMR transitions. There are two sets of crystallographically inequivalent K^+ ions: K(1) and K(2). From these angular dependences, all lead to different values for the quadrupole coupling constant and asymmetry parameter: $e^2qQ/h = 1.06 \pm 0.07$ MHz, $\eta = 0.58 \pm 0.05$ for the K(1) ion, and $e^2qQ/h = 1.45 \pm 0.07$ MHz, $\eta = 0.85 \pm 0.05$ for the K(2) ion. The EFG tensors of K(1) and K(2) are asymmetric and the orientations of the principal axes of the EFG tensors do not coincide for the K(1) and K(2) sites. The K(1) ions surrounded by nine oxygen atoms are high in symmetry, while K(2) ions surrounded by nine oxygen atoms show low symmetry.

1. Introduction

The hydrogen sulphate family, MHSO_4 ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and NH_4) has received much attention owing to its interesting properties [1]. The most interesting ion in the crystal structures of this series is the HSO_4 ion, which is usually distorted and arranged in a tetrahedral symmetry. Furthermore, the hydrogen sulphate ion, HSO_4 is connected with short hydrogen bonds. Potassium hydrogen sulphate, KHSO_4 , is a member of the alkali acid sulphates which generally are interesting due to their ferroelectric behaviour [2]. However, KHSO_4 does not show ferroelectric properties. Until now, the phase transition temperature in KHSO_4 crystal was not exactly established. Rogers and Ubbelohde [3] observed two breaks in the conductivity plot: one around 95°C and the other around 170°C . The two breaks were possibly due to the occurrence of some phase transitions. According to the Gerlich and Siegert [4] their results indicated the absence of any phase transition in this short range of temperature. Bridgman [5] reported two transitions at 164.2°C and 180°C . According to Sharon and Kalia [6], KHSO_4 is a

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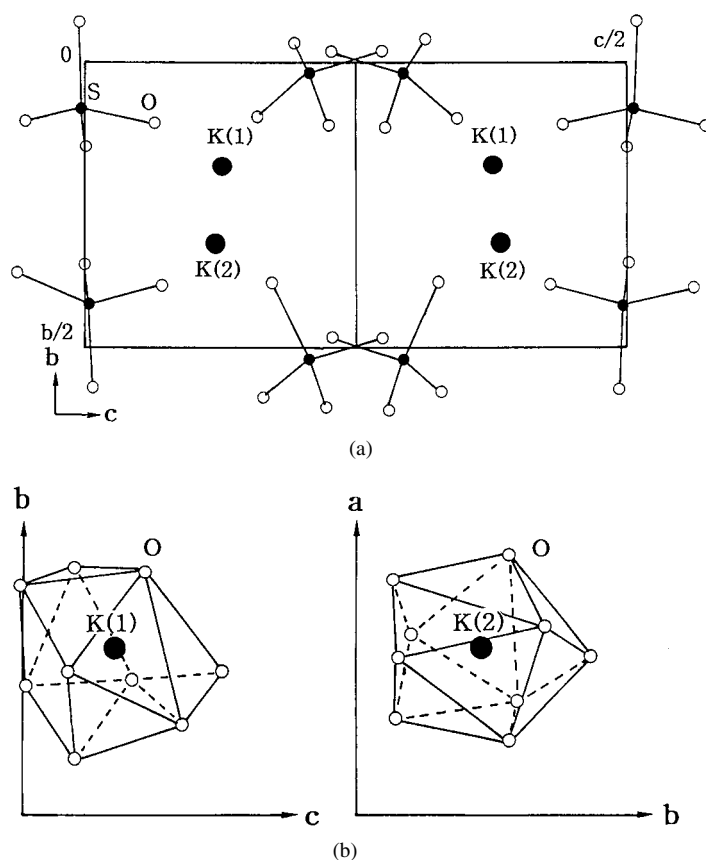


Figure 1. (a) Projection of the structure of KHSO_4 along the $[100]$ plane. The protons are not shown. (b) Surroundings of potassium ions: around K(1) in projection along the a -axis; around K(2) in projection along the c -axis.

pure protonic conductor and exhibits structural phase transitions in the vicinity of $170\text{--}180^\circ\text{C}$. Kandil *et al* [7] found a phase transition at 195°C . KHSO_4 crystals have been studied by x-ray diffraction [8], EPR [9–12] and Raman scattering measurements [13–15]. Bastow [16] has made a ^{39}K powder NMR analysis in KHSO_4 at room temperature. According to his result, the quadrupole coupling constants are $e^2qQ/h = 0.61\text{ MHz}$ and $e^2qQ/h = 1.22\text{ MHz}$, and asymmetry parameters are $\eta = 0.356$ and $\eta \simeq 1$ for K(1) and K(2), respectively. According to Poplett and Smith [17], the ^{39}K quadrupole parameter in KHSO_4 was calculated by the point-charge model: the quadrupole coupling constant and asymmetry parameter are $e^2qQ/h = 1.03\text{ MHz}$ and $\eta = 0.321$ for K(1), and $e^2qQ/h = 0.84\text{ MHz}$ and $\eta = 0.847$ for K(2), respectively. Very few NMR studies relating to the dynamic motion of oxygen atoms have been reported [18]. ^{39}K NMR studies in a KHSO_4 single crystal have not been reported until now. We performed ^{39}K NMR in a field of $B_0 = 9.4\text{ T}$ corresponding to the ^{39}K Larmor frequency of 18.672 MHz .

In this paper, we discuss the ^{39}K nuclear magnetic resonance (NMR) in a KHSO_4 single crystal grown by the slow evaporation method. The quadrupole coupling constant, the asymmetry parameter, and the direction of the principal axes of the electric field gradient (EFG) tensor of ^{39}K ($I = 3/2$) were determined at room temperature. These results show that the K(1) and K(2) sites surrounded by nine oxygen atoms are clearly distinguished by ^{39}K NMR.

Table 1. The K–O bond lengths for K(1) and K(2) in KHSO₄.

Bond type	Bond length (Å)	Bond type	Bond length (Å)
K(1)–O	2.86	K(2)–O	2.88
K(1)–O	2.95	K(2)–O	2.81
K(1)–O	2.98	K(2)–O	2.97
K(1)–O	3.02	K(2)–O	3.02
K(1)–O	3.06	K(2)–O	2.88
K(1)–O	2.96	K(2)–O	2.91
K(1)–O	2.68	K(2)–O	2.64
K(1)–O	2.82	K(2)–O	2.58
K(1)–O	2.69	K(2)–O	2.73
average K(1)–O	2.89	average K(2)–O	2.82

2. Crystal structure

The single crystal structure of KHSO₄ is orthorhombic with space group *Pbca* (D_{2h}^{15}) and 16 molecules per unit cell. The unit cell parameters are $a = 8.4030$ Å, $b = 9.799$ Å and $c = 18.945$ Å [8]. The projection of the structure of KHSO₄ along [100] is shown in figure 1(a). All the 16 K⁺ and 16 HSO₄[−] ions in the unit cell occupy sites of C₁ symmetry. There are two types of crystallographically different K⁺ as well as HSO₄[−] ions in the cell. Both potassium atoms are surrounded by nine oxygen atoms as shown in figure 1(b); eight of these form a strongly deformed antiprism, with the ninth oxygen on top of one of the squares [19]. The K–O distances for K(1) and K(2) are given in table 1. Crystal structure data shows that one kind of HSO₄[−] ion appears to form a chain of similar units, whereas two units of the other kind of HSO₄[−] ion occupy positions at opposite sides of a point of inversion forming a dimer through two intermolecular H bonds [1].

3. Experiment

Single crystals of KHSO₄ were grown by slow evaporation at room temperature of an aqueous solution containing the stoichiometric proportion of K₂SO₄ and H₂SO₄. The hexagonal-shaped crystals were colourless, transparent and of good optical quality, and their dimensions were usually 8 × 8 mm² in area and 3 mm in thickness.

Nuclear magnetic resonance signals of ³⁹K in the KHSO₄ single crystal were measured using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute in Taejeon. The static magnetic field was 9.4 T and the central radio frequency was set at $\omega_0/2\pi = 18.672$ MHz. The NMR spectra of ³⁹K were recorded with a sequence of one 90° pulse, 800 scans and a repetition time of 1 s. A ring-down delay time of 3 μs was used to remove the effect of the pulse. The angular variations of the spectra were obtained by rotating the crystal about three mutually perpendicular axes, which in turn were normal to the three mutually perpendicular planes of the crystal.

4. Experimental results and analysis

The Hamiltonian for the NMR to analyse the experimental results is the usual [20, 21]

$$H = H_Z + H_Q$$

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction. The Hamiltonian in a principal axis system of the EFG tensor is given by

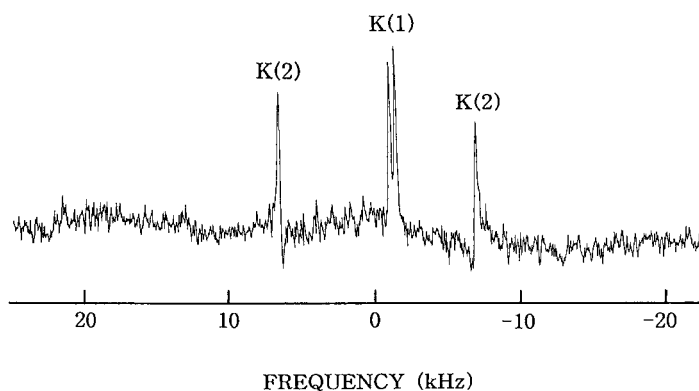


Figure 2. NMR spectrum of ^{39}K in a KHSO_4 crystal recorded with the pulse NMR spectrometer. The static magnetic field B_0 is parallel to the $(a + 30^\circ)$ -axis in the ac -plane.

$$\begin{aligned}
 H = & -\gamma\hbar\mathbf{B}_0 \cdot \mathbf{I} + e^2qQ/4I(2I - 1)[1/2\{3I_z^2 - I(I + 1)\}(3\cos^2\theta - 1) \\
 & + \eta\sin^2\theta\cos 2\varphi] + 1/4(I_+^2 + I_-^2)\{3\sin^2\theta + \eta\cos 2\varphi(1 + \cos^2\theta)\} \\
 & + 1/4\{(I_+ + I_-)I_z + I_z(I_+ + I_-)\}(6\sin\theta\cos\theta - \eta\sin^2\theta\cos 2\varphi) \\
 & - \eta/2i(I_+^2 - I_-^2)\cos\theta\sin 2\varphi + \eta/2i\{(I_+ - I_-)I_z + I_z(I_+ - I_-)\}\sin\theta\sin 2\varphi]
 \end{aligned}
 \tag{1}$$

where e^2qQ/h is the quadrupole coupling constant and η is the asymmetry parameter. Conventionally, the X , Y and Z axes are such that $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}| = eq$; then $0 \leq \eta \leq 1$. The matrix form of the spin Hamiltonian of equation (1) is employed to calculate the resonance fields with the magnetic field applied along a general direction. All resonance spectra and parameters were calculated by numerically diagonalizing the matrix using a computer program. The program used also included the Eulerian transformation of the magnetic field vector with respect to the coordinate system made of principal axes of the electric field gradient (EFG) tensor. The Eulerian angles, Φ , Θ and Ψ are for a transformation of the crystal system (a, b, c) into the EFG system (X, Y, Z) .

NMR spectra of ^{39}K in a KHSO_4 crystal at room temperature are shown in figure 2. The zero point in figure 2 corresponds to the resonance frequency 18.672 MHz of the ^{39}K nucleus. The intensities of the four resonance lines are similar. Figure 3 shows the angular dependence of the second-order quadrupole shifts of the ^{39}K resonance line in a KHSO_4 single crystal at room temperature. Dots correspond to the experimental values and full curves were obtained by fitting these data to symmetric second rank EFG tensors. These rotation patterns indicate strongly anisotropic EFG tensors. Instead of the one central resonance line of the ^{39}K nucleus, four sets of resonance lines are shown in figure 3. When the crystal is rotated about the crystallographic axis, pairs of magnetically inequivalent, but crystallographically equivalent nuclei give rise to one common line. In the case of the KHSO_4 crystal, the ^{39}K spectrum consists of four resonance lines. This result points to the existence of two types of crystallographically inequivalent K(1) and K(2). The ^{39}K spectrum consists of four resonance lines: two from K(1) and two for K(2) ions. The shifts of these two groups, one smaller and the other larger, represent the transitions of ^{39}K NMR lines due to K(1) and K(2), respectively. Based on the angular dependence of the second-order quadrupole shift in the central transition of ^{39}K NMR, two different K resonance groups, recorded with

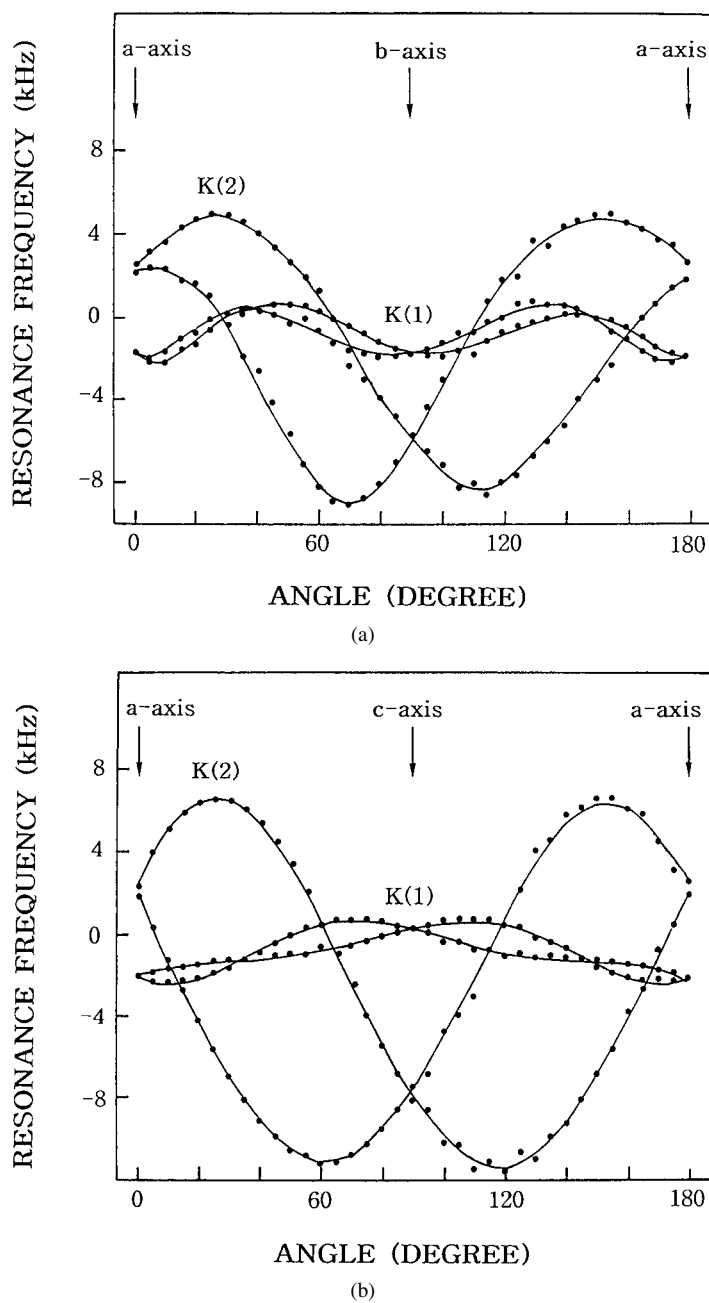


Figure 3. Rotation pattern of ³⁹K NMR measured in the *ab*- and *ca*-planes at room temperature.

different magnitudes of quadrupole coupling constant and asymmetry parameter were analysed. The quadrupole coupling constant and asymmetry parameter obtained for K(1) with smaller transition are $e^2qQ/h = 1.06 \pm 0.07$ MHz and $\eta = 0.58 \pm 0.05$. Those for K(2), and with larger transition are $e^2qQ/h = 1.45 \pm 0.07$ MHz and $\eta = 0.85 \pm 0.05$. Therefore, the EFG tensors of K(1) and K(2) are asymmetric; potassium ions are surrounded by oxygen atoms

Table 2. Quadrupole parameters of ^{39}K in KHSO_4 and LiKSO_4 crystals.

	Nucleus	e^2qQ/h (MHz)	η	Temperature (K)	Reference
KHSO_4	K(1)	1.06 ± 0.07	0.58 ± 0.05	300	present work
	K(2)	1.45 ± 0.07	0.85 ± 0.05	300	present work
LiKSO_4	K	1.49 ± 0.05	0.73 ± 0.03	180	[22]

located on a distorted SO_4 tetrahedron. Directions of the principal EFG tensor for the K ions are represented with the Eulerian angles $\Phi = 35.6^\circ$, $\Theta = 40.7^\circ$ and $\Psi = 10.2^\circ$ for K(1), and $\Phi = 23.8^\circ$, $\Theta = 61.6^\circ$ and $\Psi = 134.5^\circ$ for K(2), respectively. Parameters for the ^{39}K nucleus in a KHSO_4 crystal at 300 K were similar to those for the ^{39}K nucleus in a LiKSO_4 crystal at 180 K [22]. This similarity is consistent with the fact that KHSO_4 and LiKSO_4 single crystals have isomorphous structure; the K^+ ions in both crystals are surrounded by nine sulphate oxygen atoms. These results are summarized in table 2, together with the previous report.

5. Discussion and conclusion

The ^{39}K NMR in a KHSO_4 single crystal grown by the slow evaporation method was investigated by employing a Bruker FT NMR spectrometer. The symmetry of the crystal at room temperature is $Pbca$, which implies that there are inversion symmetries. Even though the unit cell contains 16 K^+ molecular units, the ^{39}K nuclei superposed by the inversion symmetry operation are equivalent to one another from the viewpoint of nuclear magnetic resonance. Therefore, only four central lines are observed for the arbitrary direction of the magnetic field. Four ^{39}K central lines showed the angular dependences of second-order quadrupolar shifts. From these angular dependences, all parameters were determined, and all lead to different values for the quadrupole coupling constant and asymmetry parameter. The EFG tensors of K(1) and K(2) are both asymmetric and the orientations of the principal axes of the EFG tensor do not coincide for the K(1) and K(2) sites. There are two sets of crystallographically inequivalent K^+ ions, K(1) and K(2). Because K(2) is surrounded less symmetrically by fewer and nearer ligands than K(1), the quadrupole coupling constant and the asymmetry parameter of K(1) are smaller than that of K(2). This is qualitatively consistent with the longer bond length of K(1)–O (average 2.89 Å) and the shorter K(2)–O (average 2.82 Å) bond. The K(1) ions surrounded by nine oxygen atoms are high in symmetry, while K(2) ions surrounded by nine oxygen atoms show low symmetry. Therefore, the K(1) and K(2) atoms surrounded by nine oxygen atoms located on the distorted SO_4 tetrahedron are clearly distinguished by ^{39}K NMR results.

The ^{39}K NMR results in a KHSO_4 single crystal grown by the slow evaporation method are not consistent with the quadrupole parameter obtained by Bastow [16] using the powder sample, and are consistent with the value of the quadrupole parameters for the K(1) site obtained by the point-charge model. Therefore, we think that the quadrupole parameters produced by ions surrounding the resonant nucleus in a single crystal could be obtained clearly compared with the results of the powder sample. Further studies on the phase transition are currently being conducted using the ^{39}K and ^1H spin–lattice relaxation time.

Acknowledgment

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