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^{1}H and ^{39}K Nuclear Magnetic Resonance Relaxation Study in a $KHSO_4$ Single Crystal

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Proton conducting solids are of potential interest for fuel cells, steam electrolysis, and as sensors. Proton conduction occurs in several types of materials including many hydrogen-bonded systems. In some ferroelectric and ferroelastic hydrogen-bonded crystals the superionic conductivity was discovered: $MHSO_4$ (M = K, Rb, Cs, NH_4) exhibit high proton conductivity in their high temperature phases. The hydrogen sulfate family, $MHSO_4$ has received much attention owing to its interesting properties.[1)] The most interesting group in the crystal structures of this series is the HSO_4 ion, which is usually distorted and arranged, in a tetrahedral symmetry. Potassium hydrogen sulfate, $KHSO_4$, is a member of the alkali acid sulfate family interesting because of its ferroelectric behavior.[2)] Until now, the phase transition temperature in the $KHSO_4$ crystal has not been exactly established.[3–5)]

The structure of a $KHSO_4$ single crystal is orthorhombic with space group *Pbca* (D_{2h}^{15}) and with sixteen molecules per unit cell. The unit cell parameters are $a = 8.4030$ Å, $b = 9.799$ Å, and $c = 18.945$ Å.[6)] All the 16 K^+ and 16 HSO_4^- ions in the unit cell occupy sites of C_1 symmetry. There are two types of crystallographically different K^+, as well as HSO_4^-, ions in the cell. According to the crystal structure data, one kind of HSO_4^- ion appears to form a chain of similar units whereas two units of the other kind of HSO_4^- ion occupy positions at opposite sides of a point of inversion, forming a dimer through two intermolecular H-bonds.[1)]

Recently, we reported on the ^{39}K nuclear magnetic resonance (NMR) at room temperature. The EFG tensors of K(1) and K(2) were asymmetric and the orientations of the principal axes of the EFG tensors did not coincide for the K(1) and K(2) sites. These results show that the K(1) and the K(2) sites, which are surrounded by nine oxygen atoms, were clearly distinguished by ^{39}K NMR.[7)] $KHSO_4$ crystals have previously been studied by means of X-ray diffraction,[6,8)] electron paramagnetic resonance[9–12)] and Raman scattering measurements.[13–15)]

In order to obtain information about the dynamic motions of the HSO_4 ion, it is necessary to measure the spin–lattice relaxation times, T_1, of ^{1}H and ^{39}K in $KHSO_4$ single crystals. However, very few NMR studies relating to the dynamic motion of the oxygen atoms have been reported.[16)] In this paper, the temperature dependences of the spin–lattice relaxation time, T_1, for the ^{1}H and the ^{39}K nuclei in a $KHSO_4$ single crystal grown by using the slow evaporation method were investigated using a pulse NMR spectrometer. The relaxation times of the ^{1}H and the ^{39}K nuclei in a $KHSO_4$ single crystal are new observations.

Single crystals of $KHSO_4$ were grown at room temperature by using slow evaporation of an aqueous solution containing a stoichiomeric proportion of K_2SO_4 and H_2SO_4. The crystals with hexagonal shapes were colorless and transparent and had good optical quality. The NMR signals of ^{1}H and ^{39}K in the $KHSO_4$ crystal were measured using the Bruker MSL 200 FT NMR and the Bruker DSX 400 FT NMR spectrometers, respectively, at the Korea Basic Science Institute.

The ^{1}H spin–lattice relaxation time was measured in the temperature range from 140 K to 400 K at a frequency of 200 MHz. The spin–lattice relaxation time, T_1, was measured by applying a pulse sequence of 180°–t–90°. The nuclear magnetization $S(t)$ of ^{1}H at time t after the 180° pulse was determined from the inversion recovery sequence following the pulse. The recovery traces of the magnetization of the crystals were measured at several different temperatures. The recovery traces of ^{1}H show a single exponential function. The temperature dependence of T_1 for ^{1}H in the single crystal is shown in Fig. 1. In the case of the ^{1}H nucleus, the spin–lattice relaxation time is long with $T_1 = 382$ s at room temperature. The variation of the relaxation rate, T_1^{-1}, with temperature exhibits a minimum. As the temperature is increased, the ^{1}H relaxation rate slowly decreases, and then begins to increase, passing through a minimum at 210 K. The curve of T_1^{-1} in this temperature range has a positive parabolic shape with a minimum near 210 K. This result is not consistent with the trend of ^{1}H in the hydrogen sulfate family: the shape of T_1^{-1} for ^{1}H has a positive parabolic shape in $KHSO_4$ while the plots of T_1^{-1} for ^{1}H in $RbHSO_4$ and NH_4HSO_4 crystals[17,18)] have a negative parabolic shape. Therefore, by the Bloembergen–Purcell–Pound (BPP) theory,[19)] the change in the slope of T_1 for ^{1}H in $KHSO_4$ at about 210 K is not believed to be related to HSO_4 motion. The trend of ^{1}H in $KHSO_4$ crystals is not usual. In order to check the phase transition temperature, we measured differential scanning calorimetry (DSC) using a Du Pont 2010 DSC instrument measurements. From this result, $KHSO_4$ showed four phase transitions in the temperature range from 140 K to 473 K: 451, 453, 456, and 462 K.

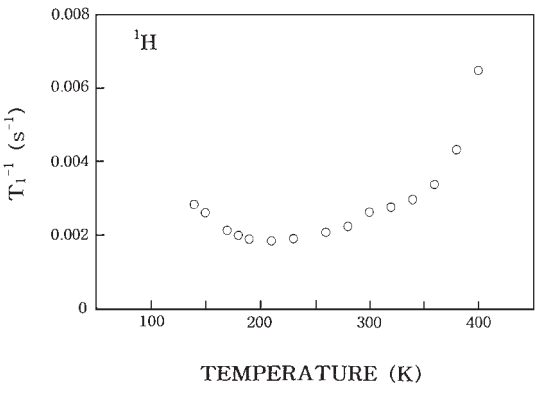

Fig. 1. Temperature dependence of the spin–lattice relaxation rate, T_1^{-1}, for ^{1}H in a $KHSO_4$ single crystal.

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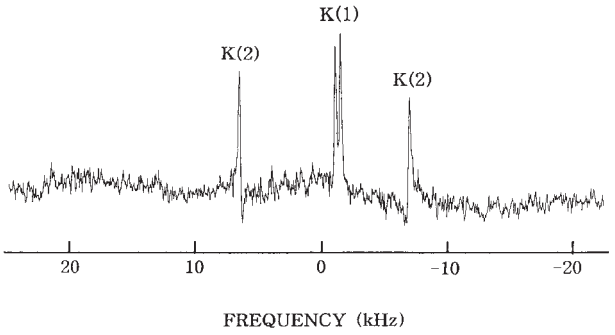

Fig. 2. NMR spectrum of ^{39}K in a $KHSO_4$ single crystal.

The NMR spectra of ^{39}K in a $KHSO_4$ crystal at room temperature are shown in Fig. 2. The zero point in Fig. 2 corresponds to the resonance frequency 18.672 MHz of the ^{39}K nucleus, and the intensities of the four resonance lines are similar. Figure represents the central transition $(+1/2 \leftrightarrow -1/2)$ of ^{39}K NMR. The satellite lines for ^{39}K nucleus, which correspond to the transitions $(-3/2 \leftrightarrow -1/2)$ and $(+1/2 \leftrightarrow +3/2)$ are out of range. Instead of the one central resonance line of the ^{39}K nucleus, four central resonance lines obtained in the case of the $KHSO_4$ crystal. This result points to the existence of two types of crystallographically inequivalent K(1) and K(2). The four central resonance lines correspond to two resonances in the K(1) nucleus and two resonances in the K(2) nucleus, all of which are caused by magnetically inequivalent sites.[7)]

The recovery traces of ^{39}K were obtained as a function of time t at several temperatures and a frequency of 18.672 MHz. These traces are explained by a single exponential function. The temperature dependence of the nuclear spin–lattice relaxation rate, T_1^{-1}, for ^{39}K is shown in Fig. 3. The values of T_1 for the four resonance lines of the ^{39}K nucleus are very similar, within the error range. The spin–lattice relaxation times are short: $T_1 = 287$ ms and $T_1 = 2846$ ms at 400 K and 200 K, respectively. The temperature dependence of the relaxation rate for ^{39}K is proportional to the T^2 as shown by solid line in Fig. 3, so based on the above theory and the experimental results, the relaxation behavior of ^{39}K in $KHSO_4$ single crystals can be explained by the Raman process. In simple NMR theory, the

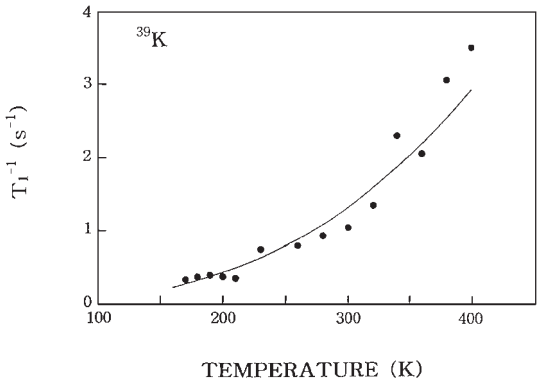

Fig. 3. Temperature dependence of the spin–lattice relaxation rate, T_1^{-1}, for ^{39}K in a $KHSO_4$ single crystal.

spin–lattice relaxation rate for random motions of the Arrhenius type with a correlation time τ_c is described in terms of fast motion regime in the temperature range of 160 K to 400 K. The fast motion region can be described as $\omega_0\tau_c \ll 1$, $T_1^{-1} \sim \exp[E_a/RT]$, where ω_0 is Larmor frequency and E_a is the activation energy. The activation energy obtained from portions of the $\log T_1$ vs 1000/T curve in this temperature range was 5.65 kJ/mol.

The spin–lattice relaxation time for the ^1H nucleus is relatively long over the entire temperature range while that for the ^{39}K nucleus is short. Based on the BPP theory, the change in the slope of T_1 for ^1H in $KHSO_4$ at about 210 K is not believed to have anything to do with HSO_4 motion. The change in the curve of the ^1H spin–lattice relaxation time near 210 K is still not completely understood. The ^{39}K spin–lattice relaxation behavior is dominated by a phonon mechanism. The temperature dependence in Fig. 3 can be described with the simple power law $T_1^{-1} = A + BT^k$.[20)] Least-squares fits for our data gave a value of $k = 2$ for the ^{39}K nucleus. Among the phonon processes, the Raman process with $k = 2$ is considered to be more effective than the direct process for nuclear quadrupole relaxation. The temperature dependence of the relaxation rate is in accordance with that for the Raman process of nuclear spin–lattice relaxation. The ^1H and the ^{39}K NMR results from the $KHSO_4$ crystals used here did not show any phase transition between 140 K and 400 K. Consequently, $KHSO_4$ single crystals may have different properties, which of them are related to defects and impurities etc.

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