

Ordering of the O(2)···D···O(2) bonds near the phase transition in $\text{KD}_3(\text{SeO}_3)_2$ single crystals by D nuclear magnetic resonance

Research Article

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Abstract:

Deuterium resonance investigations of $\text{KD}_3(\text{SeO}_3)_2$ single crystals have been performed near the phase transition temperature T_C . There are two types of deuterium bonds in these crystals with different behaviors at this phase transition. Our experimental results show that there are significant changes in the D spin-lattice relaxation time T_1 at T_C ; the abrupt decrease in T_1 near T_C can be explained by the critical slowing down of an overdamped soft pseudospin-type deuteron mode. Further, the ordering of the O(2)···D···O(2) bonds is affected by the phase transition, whereas the ordering of the O(1)–D···O(3) bonds is unaffected. The D NMR measurements also show that the D(2) deuteron disordering above T_C is dynamic and not static.

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1. Introduction

The ferroelectric behavior of some hydrogen-bonded crystals has been attributed to the ordered arrangement of the protons involved in their hydrogen bonds. The family of alkali trihydrogen selenite crystals of the type $\text{MeH}_3(\text{SeO}_3)_2$ (Me=Li, Na, K, Rb, Cs, and NH_4) is one of the most interesting families of hydrogen-bonded systems

because of their structural peculiarities and physical properties (see, for example, Gorbatyi et al. [1], Zapart et al. [2], Sakai and Tatsuzaki [3]). In particular, the alkali metal trihydrogen selenites are an important group of hydrogen-bonded ferroelectrics that have very interesting properties. The crystals of the trihydrogen selenite family have no isomorphous structures, but the polar SeO_3^{2-} groups are always linked by hydrogen bonds. The significant isotope effects on the phase transition temperatures, especially of the Na, K, and Cs trihydrogen selenites, demonstrate the significance of the H-bond network. However, $\text{KH}_3(\text{SeO}_3)_2$ is unique in this family of compounds be-

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cause it does not exhibit any ferroelectric or antiferroelectric effects by Huvalov et al. [4]. In this substance, there is a large difference between the phase transition temperatures T_C of the hydrogen compound $\text{KH}_3(\text{SeO}_3)_2$ and the deuterated compound $\text{KD}_3(\text{SeO}_3)_2$ (see, for example, Huvalov et al. [4], Ivanov et al. [5], Yagi and Tatsuzaki [6], Makita et al. [7], Grande et al. [8], Kasahara [9], Tanaka et al. [10], Makita et al. [11], and Ivanov [12]). T_C of $\text{KH}_3(\text{SeO}_3)_2$ is 211 K and that of $\text{KD}_3(\text{SeO}_3)_2$ is 302 K. This large isotope effect suggests that the deuterium bond plays an important role in the phase transition of $\text{KD}_3(\text{SeO}_3)_2$.

By using nuclear magnetic resonance (NMR), Grande et al. [8] and Kasahara [9] determined the quadrupole parameters and the change in the principal axes of the electric field gradient (EFG) at the deuterium sites of $\text{KD}_3(\text{SeO}_3)_2$ below and above T_C for the $\text{O}(1)\cdots\text{D}\cdots\text{O}(3)$ and $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ bonds. They concluded that the disordered $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ bonds become ordered below T_C . Blinc et al. [13, 14] investigated D spin-lattice relaxation in $\text{KD}_3(\text{SeO}_3)_2$ and concluded that there is a slowing down of the overdamped soft pseudospin-type deuteron mode. They also obtained the ^{17}O -proton nuclear double-resonance spectra of $\text{KH}_3(\text{SeO}_3)_2$ below and above the ferroelastic transition and the quadrupole coupling constants of all chemically inequivalent oxygen sites. Although a D NMR study of $\text{KD}_3(\text{SeO}_3)_2$ crystals has previously been reported, the order-disorder phase transition of $\text{KD}_3(\text{SeO}_3)_2$ has not yet been investigated in detail by using D NMR.

As protons are expected to play a dominant role in the physical properties and phase transition mechanisms of hydrogen-bonded crystals, probing the crystals deuterium motions with D NMR is expected to be a powerful means of studying their microscopic nature. The link between the dynamical transfer of deuterium atoms and structural phase transitions is the subject of keen interest. In order to investigate the role of hydrogen bonds in $\text{KH}_3(\text{SeO}_3)_2$, we grew $\text{KD}_3(\text{SeO}_3)_2$ single crystals; we then performed a deuteron magnetic resonance study of the single crystals to determine the effects of the phase transition on the deuterium bonds and on the motions of the deuterium atoms in the deuterium bonds. Further, the temperature dependences of the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 were measured near the phase transition temperature. The purpose of this study was to illuminate the nature of this phase transition by using deuteron NMR spin-lattice relaxation and spin-spin relaxation time measurements to reveal the deuteron dynamics.

2. Crystal structure

$\text{KD}_3(\text{SeO}_3)_2$ undergoes a second-order phase transition from a high-temperature orthorhombic phase to a low-temperature monoclinic phase at $T_C=302$ K. At room temperature, the structure of $\text{KH}_3(\text{SeO}_3)_2$ belongs to the space group Pbcn (D_{2h}^{14}) of the orthorhombic system (Garland et al. [15] and Gorbatyi et al. [16]). The orthorhombic unit cell of $\text{KH}_3(\text{SeO}_3)_2$ crystals at room temperature has the lattice parameters $a=16.152$ Å, $b=6.249$ Å, and $c=6.307$ Å (see, for example, Gorbatyi et al. [16], Hansen et al. [17]), and contains four formula units. The unit cell dimensions of $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ crystals are the same within experimental error; the crystal structures of the undeuterated and deuterated compounds are isomorphous. Below T_C , the crystal is monoclinic and belongs to the centrosymmetric space group $\text{P}2_1/\text{b}$ (C_{2h}^5) (see, for example, Makita et al. [7], Lehmann and Larsen [18], and Iwata et al. [19]) with no superlattice structure. At low temperatures, the unit cell parameters are $a=16.130$ Å, $b=6.206$ Å, $c=6.257$ Å, and $\alpha=91.2^\circ$ as reported by Makita et al. [7]. Half of the unit cell of the high temperature phase is shown schematically in Fig. 1. $\text{KD}_3(\text{SeO}_3)_2$ contains two types of deuterium sites; the SeO_3 groups are linked by two different types of $\text{O}\cdots\text{O}$ bonds. The asymmetric $\text{O}(1)\cdots\text{O}(3)$ bonds (D(1)-bonds), in which the deuteriums are located near the O(3) oxygens, form zig-zag shaped chains along the c -axis, are ordered above the below T_C . On the other hand, the asymmetric $\text{O}(2)\cdots\text{O}(2)$ bonds (D(2)-bonds), which are directed along the a -axis, are assumed to be disordered above T_C and ordered below T_C as proposed by Lehmann and Larsen [18].

3. Experimental method

The single crystals of $\text{KD}_3(\text{SeO}_3)_2$ were grown by carrying out the slow evaporation method from a D_2O solution of one mole of K_2CO_3 and four moles of SeO_2 . Single crystals of $\text{KD}_3(\text{SeO}_3)_2$ were grown by gradual cooling of the saturated solution at a rate of about 0.1° a day. The crystals are long and thin, colorless and transparent, plates that are approximately $7 \times 3 \times 1.5$ mm³ in size. The phase transition temperature varies according to the substitution of deuterium in this crystal: for 100% substitution, T_C is 302 K (see, for example, Yagi and Tatsuzaki [6] and Tanaka et al. [10], for 93~96% substitution T_C is 298 K (see, for example, Huvalov et al. [4], Yagi and Tatsuzaki [6], and Kasahara [9]), and for a deuterium substitution of ~80%, T_C is 286.8 K as reported by Makita et al. [11]. To determine the phase transition tem-

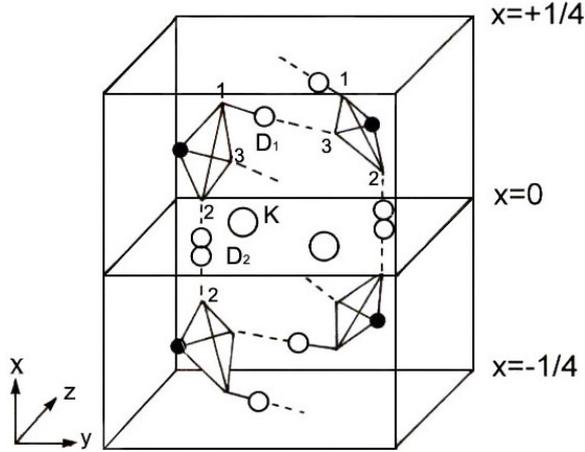


Figure 1. The structure of the KD₃(SeO₃)₂ crystal in the high temperature phase. Half of the unit cell is shown. Tetrahedral SeO₃ molecules are connected by ordered deuteriums D(1) in zig-zag chains, and D(2) is disordered in this phase.

peratures of the KD₃(SeO₃)₂ crystals, differential scanning calorimetry (DSC) was carried out on the crystals by using a DuPont 2010 DSC instrument. The measurements were performed at a heating rate of 10 K/min for temperatures between 120 K and 600 K. It was found that KD₃(SeO₃)₂ undergoes a phase transition near 302 K and melts at 350 K. The phase transition temperature of 302 K obtained in our laboratory is consistent with the result of Tanaka et al. [10].

The NMR signals of the D nuclei in the KD₃(SeO₃)₂ single crystals were measured by using the Bruker 400 FT NMR spectrometers at the Korea Basic Science Institute. The static magnetic field was 9.4 T, and the central radio frequency was set at $\omega_0/2\pi=61.424$ MHz for the D nucleus. For the D T_1 measurements, a $\pi-t-\pi/2$ pulse sequence was used. In addition, T_2 was measured using the solid echo method. The width of the π pulse was 16.65 μ s for D. The temperature-dependent NMR measurements were obtained over the temperature range 240~410 K. The samples were maintained at a constant temperature (accuracy ± 0.5 K) by controlling the nitrogen gas flow and the heater current.

4. Experimental results and analysis

A deuteron with spin $I = 1$ in a KD₃(SeO₃)₂ single crystal has three energy levels, namely 1, 0, and -1 , in an external magnetic field. The transition probabilities for $\Delta m = \pm 1$ and $\Delta m = \pm 2$ are denoted P_1 and P_2 respectively. In

addition, the differences in population between the equilibrium value and that at time t for energy levels 1, 0, and -1 are denoted n_{-1} , n_0 , and n_1 , respectively. The population equations for the nuclear spin $I = 1$ induced by the fluctuations of the quadrupole coupling tensor are thus (see, for example Cowan [20], Igarashi et al. [21], Bonera et al. [22], and Towta and Hughes [23])

$$\begin{aligned}\frac{dn_1}{dt} &= -(P_1 + P_2)n_1 + P_1n_0 + P_2n_{-1}, \\ \frac{dn_0}{dt} &= P_1n_1 - 2P_1n_0 + P_1n_{-1}, \\ \frac{dn_{-1}}{dt} &= P_2n_1 + P_1n_0 - (P_2 + P_1)n_{-1}.\end{aligned}\quad (1)$$

The deuteron magnetization is proportional to $\sum_{m=-l}^{m=l} n_m \cdot \langle \tilde{I}_z \rangle_m = n_1 - n_{-1}$, where $m=1, 0$, and -1 , and $\langle \tilde{I}_z \rangle_m = m$. The spin-lattice relaxation time for the D nuclei is then

$$\frac{1}{T_1} = P_1 + 2P_2.\quad (2)$$

When the deuteron energy levels are not equidistant, the approach of the nonequilibrium deuteron magnetization towards equilibrium cannot in general be described by a single exponential term. In the present case, however, the deuteron relaxation data can within the limits of experimental error be represented by a single exponential term. The NMR spectrum for the D nuclei in a KD₃(SeO₃)₂ crystal was obtained as a function of temperature. A unit cell contains twelve deuteriums at room temperature, eight of which are present in O(1)~D···O(3) bonds located along the c-axis and four of which are present in O(2)···D···O(2) bonds directed along the a-axis. In other words, two different deuterium-bond chains are present in the KD₃(SeO₃)₂ crystal, so its solid-state D NMR spectrum is expected to consist of resonance lines of two types. The resonance lines of D were observed when the magnetic field was applied parallel to the a-axis of the crystals, and the D signals due to D(1) and D(2) were obtained in the temperature range 240~410 K and are shown in Fig. 2. At room temperature, the broad and narrow signals in the spectrum are due to the eight and four deuteriums per unit cell respectively, as shown in Fig. 1. These signals are assigned to D(1) and D(2) respectively. On the other hand, at high temperatures the broad and narrow signals merge into one resonance line. As temperature is raised, the integrated intensity of the D(1) signal changes slightly, whereas that of the D(2) signal increases abruptly (see Fig. 3). The D(2) signal is sharp above 350 K ($=T_m$), which indicates that D(2) play an

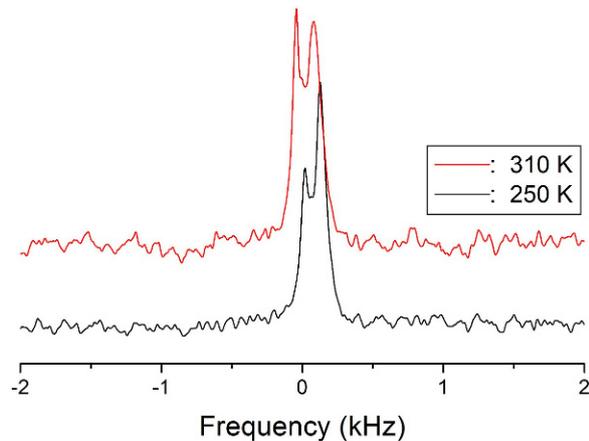


Figure 2. D NMR spectra for $\text{KD}_3(\text{SeO}_3)_2$ crystals: (a) below T_C and (b) above T_C .

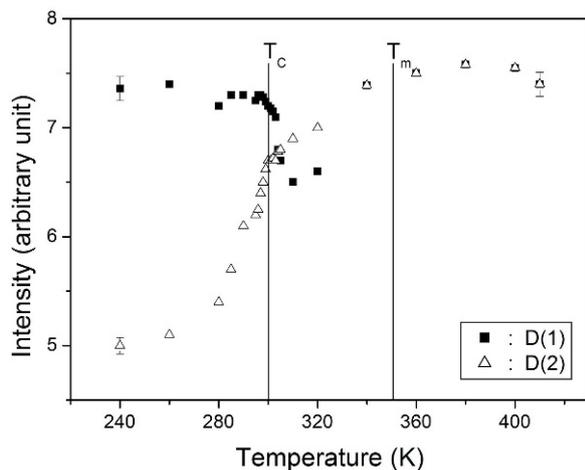


Figure 3. The integrated intensities of the D(1) and D(2) NMR signals for a $\text{KD}_3(\text{SeO}_3)_2$ crystal as functions of temperature.

important role in this temperature range. A similar result has been reported elsewhere: the dynamic ordering of deuterium occurs in one of the deuterium bonds as the material enters the phase transition. Thus, we conclude that the increase in the intensity of the signal due to D(2) in $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ with temperature is related to the ordering of such deuterons. The crystal is due to ordering of the D-atom arrangement for one of the types of deuterium bonds, and these results are consistent with those by Rozanove et al. [24].

The splitting of the D resonance lines in $\text{KD}_3(\text{SeO}_3)_2$ was obtained as a function of temperature, and the resonance points for D(2) were found to change only slightly near 300 K (see Fig. 4). Further, the resonance points shift to higher frequencies for temperatures above 350 K. These changes at 300 K and 350 K correspond to changes in the

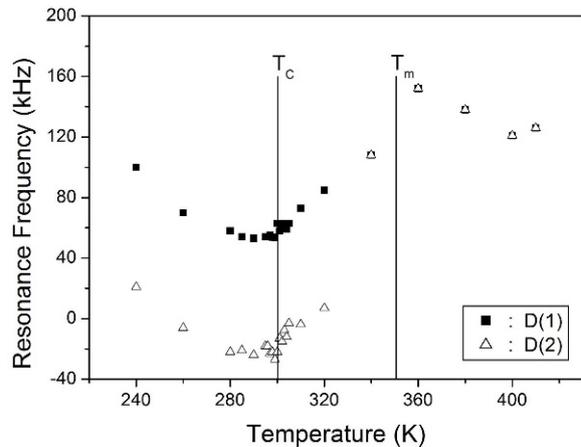


Figure 4. The resonance frequencies for the D(1) and D(2) NMR signals of a $\text{KD}_3(\text{SeO}_3)_2$ crystal as functions of temperature.

deuteron motions and to the structural rearrangements associated with the phase transition. In other words, these changes in the splitting of the D resonance lines are due to changes in local symmetry at the D sites. In other hands, the change in the splitting of the D resonance reflect changes in the local symmetry of the D sites. The variation in the splitting at high temperature indicates that the electric field gradient (EFG) at the D sites changes with temperature, which in turn means that the atoms in the neighborhood of D are displaced at the phase transition temperature. In particular, the D(2) ions play an important role in the phase transition. In addition, the number of resonance lines in the D spectrum changes from two to only one at a temperature about 10 K lower than the melting temperature. The presence of only one signal due to the D nuclei is due to the liquid state resulting from the melting of the crystal. This result is consistent with the peak at 350 K in the differential scanning calorimetry (DSC) thermogram.

The recovery traces of the magnetizations were obtained from the NMR signals of the D nuclei in the $\text{KD}_3(\text{SeO}_3)_2$ crystals at several temperatures. The recovery traces for D can be represented by using Eq. (2), but the recovery traces were determined by fitting a single exponential form at all temperatures investigated. Fig. 5 shows the inversion recovery traces for the two resonance lines of D nuclei in $\text{KD}_3(\text{SeO}_3)_2$ crystals at room temperature for delay times ranging from 1 μs to 3 s. The inversion recovery traces vary with the delay time. The temperature dependences of the spin-lattice relaxation time, T_1 , and the spin-spin relaxation time, T_2 , are shown in Figs. 6 and 7, respectively. Their temperature dependences are similar. In these figures, the symbols \blacksquare and \triangle denote the results for the $\text{O}(1)\cdots\text{D}\cdots\text{O}(3)$ bonds (D(1)-

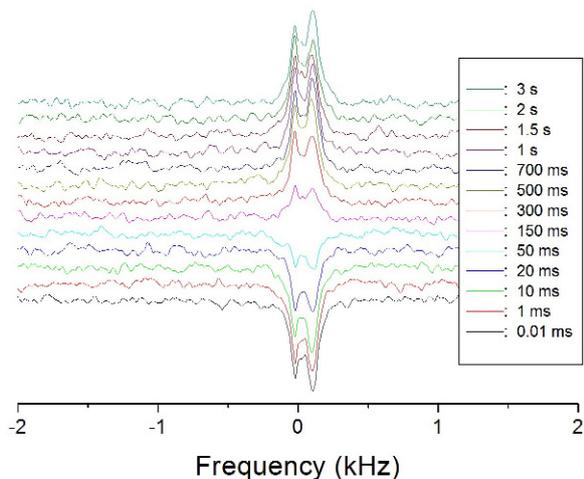


Figure 5. The inversion recovery behaviors of the D(1) and D(2) NMR signals at room temperature.

bonds) and O(2)···D···O(2) bonds (D(2)-bonds) respectively. The relaxation times of the D nuclei undergo significant changes near T_C . At room temperature, the spin-lattice relaxation times T_1 of D for the O(1)···D···O(3) and O(2)···D···O(2) bonds are 0.1 s and 0.04 s, respectively. The T_1 of D for the O(1)···D···O(3) bond is much longer than the T_1 of D for the O(2)···D···O(2) bond. Near T_C , the D(1) and D(2) spin-lattice relaxation times in $\text{KD}_3(\text{SeO}_3)_2$ with dominant quadrupole relaxation indicate the critical slowing down of an overdamped soft pseudospin-type deuteron mode. Note that the T_1 for D(2) passes through a sharp minimum value near T_C . Near the melting temperature, the T_1 of D for the O···D···O bond has very short liquid-like values. A liquid-like T_2 value indicates that there is motional averaging of the deuteron dipole-dipole interactions due to translational motion.

5. Discussion and conclusion

Deuterium resonance investigations of $\text{KD}_3(\text{SeO}_3)_2$ single crystals were performed for the low- and high-temperature phases. There are two types of deuterium bonds in this crystals with different behaviors at the phase transition. In contrast to the O(1)···D···O(3) bonds, the O(2)···D···O(2) bonds undergo an order-disorder process; it was confirmed that there are two symmetrically inequivalent deuterons D(1) and D(2) at low temperatures. The number of resonance lines in the D spectrum changes from two to only one near T_m (≈ 350 K). The presence of only one signal from the D nuclei is due to the liquid state resulting from the melting of the crystal. In addition, there are significant changes in T_1 and T_2 for

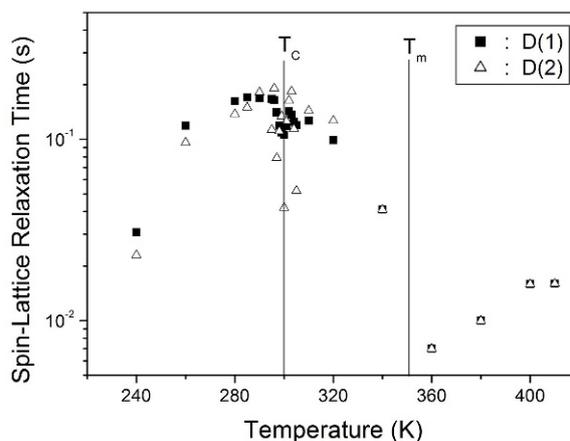


Figure 6. Temperature dependences of the spin-lattice relaxation time T_1 for D(1) and D(2) in a $\text{KD}_3(\text{SeO}_3)_2$ single crystal.

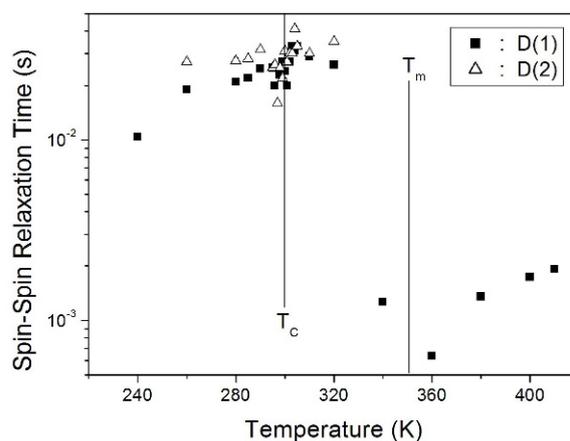


Figure 7. Temperature dependences of the spin-spin relaxation time T_2 for D(1) and D(2) in a $\text{KD}_3(\text{SeO}_3)_2$ single crystal.

D near T_C and T_m respectively. Our results show that the phase transition is associated with the ordering of the O(2)···D···O(2) bonds. At high temperatures, the T_1 and T_2 of D for the O···D···O bond are very short and liquid-like. These liquid-like values at high temperatures might be associated with the breaking of the deuterium bonds between the nearest SeO_3 groups and the formation of new weaker disordered deuterium bonds between neighboring SeO_3 groups. This behavior is expected for most hopping-type ionic conductors, and is attributed to interactions between the mobile ions and the neighboring group ions within the crystal. The deformation of the unit cell below T_C causes a change in the direction of the O(2)···D···O(2) bond, whereas the direction of the O(1)···D···O(3) bonds does not alter. The deuteron NMR measurements show that the D(2) deuteron disorder above T_C is dynamic and not static.

We now compare these NMR results for the $\text{KD}_3(\text{SeO}_3)_2$ crystal with previous results for the $\text{KH}_3(\text{SeO}_3)_2$ crystal reported by Lim and Jung [25]. In the case of $\text{KH}_3(\text{SeO}_3)_2$, there are no significant changes in T_1 and T_2 for ^1H at T_C ($=211$ K), and the role of structural changes in this transition is indeed relatively minor. In the case of $\text{KD}_3(\text{SeO}_3)_2$, the transition is driven by the deuterium in the $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ bonds, which indicates that the $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ bond plays an important role in this phase transition ($=300$ K). In our experimental results such critical effects are seen in the deuteron T_1 at T_C ; the sharp minimum in T_1 can be explained by the critical slowing down of an overdamped soft pseudospin-type deuteron mode. Further, the ordering of the $\text{O}(2)\cdots\text{D}\cdots\text{O}(2)$ bonds is connected with the phase transition mechanism, whereas the ordering of the $\text{O}(1)\cdots\text{D}\cdots\text{O}(3)$ does not alter. When hydrogen in $\text{KH}_3(\text{SeO}_3)_2$ crystal is replaced by deuterium, the deuterium atoms will occupy the same places in the lattice as the protons. The effects of deuteration of potassium trihydrogen selenite crystals include not only a shift in the phase transition temperature T_C , but also a change in the local symmetry. It is clear from the above result that the deuterium bonds in $\text{KD}_3(\text{SeO}_3)_2$ play an important role in the phase transition, as is the case for other deuterium-bonded compounds.

Acknowledgments

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References

- [1] L.W. Gorbatyi, W.I. Ponomarev, D.M. Kheiker, *Kristallografiya* 16, 899 (1971)
- [2] W. Zapart, S. Waplak, J. Stankowski, L. Shuvalov, *J. Phys. Soc. Jpn.* 44, 1600 (1978)
- [3] A. Sakai, I. Tatsuzaki, *J. Phys. Soc. Jpn.* 50, 3016 (1981)
- [4] L.A. Huvalov, N.R. Ivanov, T.K. Sitnik, *Kristallografiya* 12, 315 (1967)
- [5] N.R. Ivanov, L.A. Shuvalov, N.V. Gordeeva, *Sov. Phys. Crystallogr.* 13, 145 (1968)
- [6] T. Yagi, I. Tatsuzaki, *J. Phys. Soc. Jpn.* 26, 865 (1969)
- [7] Y. Makita, F. Sakurai, T. Osaka, I. Tatsuzaki, *J. Phys. Soc. Jpn.* 42, 518 (1977)
- [8] S. Grande, H.D. Mecke, L.A. Shuvalov, *Phys. Stat. Sol. (a)* 46, 547 (1978)
- [9] M. Kasahara, *J. Phys. Soc. Jpn.* 44, 537 (1978)
- [10] H. Tanaka, T. Yagi, I. Tatsuzaki, *J. Phys. Soc. Jpn.* 44, 1257 (1978)
- [11] T. Makita, T. Osaka, A. Miyazaki, *J. Phys. Soc. Jpn.* 44, 225 (1978)
- [12] N.R. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 43, 1706 (1979)
- [13] R. Blinc, B. Lozar, J. Slak, S. Zumer, L.A. Shuvalov, *Phys. Rev. B* 23, 6133 (1981)
- [14] J. Seliger, V. Zagar, R. Blinc, A. Novak, *J. Chem. Phys.* 84, 5857 (1986)
- [15] C.W. Garland, G. Park, I. Tatsuzaki, *Phys. Rev. B* 29, 221 (1984)
- [16] L.W. Gorbatyi, W.I. Ponomarev, D.M. Kheiker, *Sov. Phys. Crystallogr.* 16, 781 (1972)
- [17] F. Hansen, R.G. Hazell, S.E. Rasmussen, *Acta Chem. Scand.* 23, 2561 (1969)
- [18] M.S. Lehmann, F.K. Larsen, *Acta Chem. Scand.* 25, 3859 (1971)
- [19] Y. Iwata, N. Koyano, I. Shibuya, M. Tokunaga, *J. Phys. Soc. Jpn.* 47, 922 (1979)
- [20] B. Cowan, *Nuclear Magnetic Resonance and Relaxation*, Cambridge University Press, Cambridge, (1997)
- [21] M. Igarashi, H. Kitagawa, S. Takahashi, R. Yoshizak, Y. Abe, *Z. Naturforsch* 47a, 313 (1992)
- [22] G. Bonera, F. Borsa, A. Rigamonti, *Phys. Rev. B* 21, 2784 (1970)
- [23] S. Towta, D.G. Hughes, *J. Phys.: Condens. Matter* 2, 2021 (1990)
- [24] O.V. Rozanov, Yu.N. Moskvich, A.A. Sukhovskii, *Sov. Phys. Solid State* 25, 212 (1983)
- [25] A.R. Lim, W.K. Jung, *J. Phys. D: Appl. Phys.* 41, 135407 (2008)