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¹³³Cs Nuclear Magnetic Resonance Relaxation Study of the Phase Transition of Cs₂MnCl₄·2H₂O Single Crystals

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Abstract : The structural phase transition of Cs₂MnCl₄·2H₂O single crystals was investigated by determining the ¹³³Cs spin-lattice relaxation time T₁. The number of resonance lines in the ¹³³Cs spectrum changes from seven to one near 375 K, which means that above 375 K the Cs sites are symmetric. Further, the T₁ of the ¹³³Cs nucleus undergoes a significant change near 375 K, which coincides with the change in the splitting of the ¹³³Cs resonance lines. The change in T₁ near T_C is related to the loss of H₂O, and means that the forms of the octahedra of water molecules surrounding Cs⁺ are disrupted.

Keywords : Cs₂MnCl₄·2H₂O, nuclear magnetic resonance, spin-lattice relaxation time, phase transition temperature

INTRODUCTION

The crystals of dihydrate tetrahalogeno-metallates with the general formula A₂BY₄·2H₂O (A=NH₄, K, Rb, Cs; B=Cu, Mn, Ca, Ni; Y=Cl, Br) can be divided into two groups according to their symmetry and structure: one group of crystals including those with Cu²⁺ ions have tetragonal symmetry with space group 4₂/mmm, Z=2, whereas the other group of crystals including those with Mn²⁺ ions have triclinic symmetry with space group P1, Z=1. Specific heat^{1,2}, susceptibility^{3,4}, and

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nuclear magnetic resonance (NMR)⁵ studies of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals including second groups have shown that this material orders antiferromagnetically with a Neel temperature of $T_N=1.84$ K. The current interest in the magnetic behavior of this crystal stems from the fact that its structure is quite simple compared to those of most crystals that order magnetically at low temperatures⁶. $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ forms triclinic crystals with space group $\bar{P}1$. The unit cell contains one formula unit and has the dimensions $a=5.74$ Å, $b=6.66$ Å, and $c=7.27$ Å, with $\alpha=67.0^\circ$, $\beta=87.8^\circ$, and $\gamma=84.3^\circ$. The crystal structure of triclinic $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ is shown in Fig. 1.

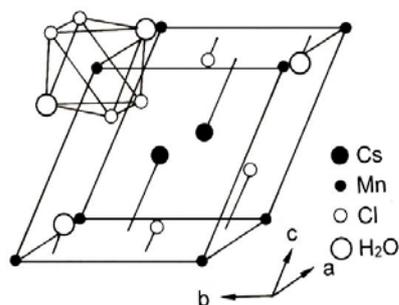


Figure. 1. The crystal structure of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ with one complete $[\text{Cl}_4 \cdot 2\text{H}_2\text{O}]$ octahedron around one Mn ion.

Each Mn^{2+} ion is surrounded by a distorted octahedron consisting of four Cl^- ions forming a nearly perfect square and two water molecules at opposite vertices of the octahedron. The $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal is isostructural with $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals⁸. The structure of the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal has until now only been studied near the Neel temperature, and sufficient research into its dynamics above room temperature has not previously been conducted.

Spence et al. [6] examined the NMR spectrum of antiferromagnetic Cs₂MnCl₄·2H₂O near the Neel temperature to determine its magnetic ordering. The electric field gradient (EFG) tensors for ¹³³Cs in Cs₂MnCl₄·2H₂O crystals have been obtained with the nuclear quadrupole resonance (NQR) method at liquid-nitrogen temperatures by Jonge et al.⁹ Recently, the ferroelastic domain structure of this crystal was briefly mentioned by Czlonkowska et al.¹⁰.

The present study determined the structure and phase transition temperature of these crystals by using X-ray diffraction and differential scanning calorimetry (DSC) respectively. Our aim was to investigate the phase transition and the structural dynamics of Cs₂MnCl₄·2H₂O crystals. To probe the crystal's structural properties, the ¹³³Cs relaxation times were determined because these relaxation times are likely be very sensitive to changes in crystal symmetry. The NMR spectrum and the spin-lattice relaxation time, T₁, for ¹³³Cs in Cs₂MnCl₄·2H₂O crystals were obtained as functions of temperature. The structural changes in Cs₂MnCl₄·2H₂O crystals were then determined, and we used these results to analyze the environments of the Cs nuclei.

EXPERIMENTAL

Cs₂MnCl₄·2H₂O crystals were obtained by performing the slow evaporation of an aqueous solution of CsCl and MnCl₂·2H₂O in the appropriate molar ratios at room temperature. The crystals are pale pink in color and prismatic in form. The structure of the Cs₂MnCl₄·2H₂O crystals at room

temperature was determined with an X-ray diffractometer system (Bruker AXS GMBH) at the Korea Basic Science Institute. The $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals have a triclinic structure with cell parameters $a=5.75 \text{ \AA}$, $b=6.75 \text{ \AA}$, and $c=7.37 \text{ \AA}$, $\alpha=65.25^\circ$, $\beta=87.45^\circ$, and $\gamma=83.88^\circ$. These values are consistent with the results of Jensen [7]. The phase transition temperature was then determined by using a DuPont 2010 DSC instrument; the measurements were performed at a heating rate of 10 K/min. An endothermic peak was observed at 375 K, as shown in Fig. 2.

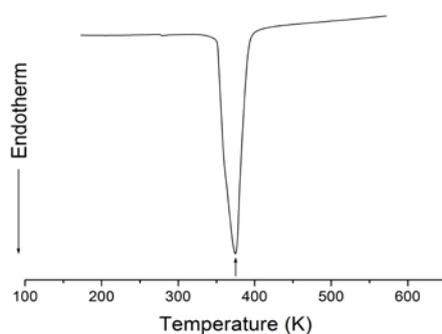


Figure. 2. The differential scanning calorimetry thermogram of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystals. The arrow indicates the phase transition temperature.

We checked for premelting and decomposition phenomena with thermogravimetric analysis (TGA). The TGA results show that the crystals undergo decomposition in the process of dehydration and lose two molecules of crystalline water at 370 K, as is consistent with the results of Czlonkowska et al.¹⁰.

The spin-lattice relaxation times of the ^{133}Cs nuclei in the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystals were

measured by using the Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 9.4 T, and the central radio frequency was set at $\omega_0/2\pi=52.485$ MHz for the ¹³³Cs nucleus. The spin-lattice relaxation times of the ¹³³Cs nuclei in the crystals were measured by applying $\pi/2-t-\pi/2$ pulse sequences. The nuclear magnetizations $S(t)$ of the ¹³³Cs nuclei at time t after the $\pi/2$ pulses were determined from the saturation recovery sequence. The temperature dependences of the NMR measurements were obtained in the temperature range 180–410 K. The temperature of each sample was held constant by controlling the nitrogen gas flow and the heater current, giving an accuracy of $\pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

The spin-lattice relaxation time, T_1 , of ¹³³Cs in Cs₂MnCl₄·2H₂O was measured in the temperature range 180–410 K. When only the central line is excited, the magnetization recovery trace of ¹³³Cs in Cs₂MnCl₄·2H₂O with dominant magnetic relaxation does not follow a single exponential function, but can be represented by a combination of four exponential functions¹¹.

$$[S(\infty) - S(t)] / S(\infty) = 0.011905 \exp(-2 Wt) + 0.068182 \exp(-12 Wt) \\ + 0.20605 \exp(-30 Wt) + 0.713868 \exp(-56 Wt) \quad (1)$$

where $S(t)$ is the nuclear magnetization corresponding to the central transition at time t , and W_1 and W_2 are the transition probabilities corresponding to $\Delta m = \pm 1$ and $\Delta m = \pm 2$, respectively. The return to equilibrium is characterized by four relaxation times. However, at higher temperatures, such as in our experiments, the spin system quickly reaches thermal equilibrium according to the spin temperature, and the relaxation can then be described with a single relaxation time T_1 . Therefore, the recovery data for high temperatures can be satisfactorily fitted by using the expression¹⁴⁻¹⁶

$$[S(\infty) - S(t)] / S(\infty) = \exp(-Wt) \quad (2)$$

with a single exponential function. The spin-lattice relaxation time for ^{133}Cs was obtained in terms of $1/W$.

The NMR spectrum of ^{133}Cs ($I=7/2$) in $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ at room temperature was obtained at a frequency $\omega_0/2\pi=52.485$ MHz, as shown in Fig. 3(a). The seven resonance lines of the ^{133}Cs NMR spectrum are a result of the quadrupole interaction of the ^{133}Cs nucleus. The ^{133}Cs NMR spectrum consists of six satellite lines and a central line; when the crystals are rotated about the crystallographic axis, crystallographically equivalent nuclei give rise to seven lines: one central line and six satellite lines. The magnetic field was applied perpendicular to the c -axis of the crystal. The splittings of the ^{133}Cs resonance lines were measured in the temperature range 180–400 K, and it was found that the distances between the satellite lines slowly decrease with increasing temperature, as

shown in Fig. 3(b). Below T_C , the splitting between the ^{133}Cs resonance lines decreases with increasing temperature. This result means that the quadrupole coupling constant of the ^{133}Cs nucleus decreases with increasing temperature. On the other hand, at low temperatures the ^{133}Cs NMR spectrum consists of 14 resonance lines in two groups, as shown in Fig. 3(b), which indicates that this crystal has the characteristics of a ferroelastic twin structure. This result supports the conclusion of an optical polarizing microscopy study that this crystal has ferroelastic properties¹⁰.

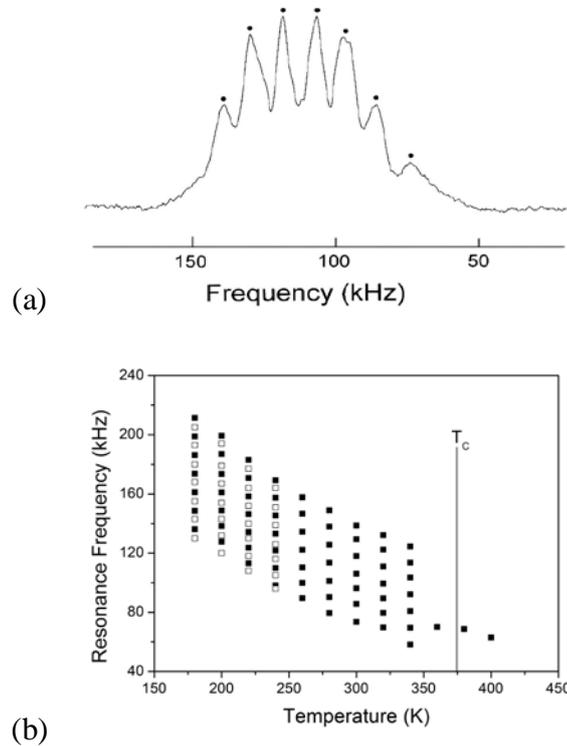


Figure 3. (a) The ^{133}Cs NMR spectrum for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystals at room temperature and (b) the splitting of the ^{133}Cs NMR spectrum for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystals as a function of temperature.

Further, the Cs spectrum is displaced to a higher frequency relative to the reference signal obtained for the ^{133}Cs line from an aqueous solution of CsCl; this shift is related to the transferred hyperfine interaction of the Mn^{2+} nuclei in the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystal, and is possibly due to dipole-dipole interactions between the magnetic moments of the Cs^+ nuclei and the magnetic moments of the Mn^{2+} atoms.

The number of resonance lines in the ^{133}Cs spectrum changes from seven to one near T_C (=375 K). Above T_C , the presence of only one ^{133}Cs resonance line indicates that the transition results in a dynamical averaging of the crystal electric field and that Cs is then apparently present in a cubic symmetry field. This result means that above T_C the Cs sites in $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ are symmetrical, as is the case for $\text{Cs}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals¹⁵. Further, the changes in the geometry of the cesium sites that arise due to the loss of H_2O around the Cs nuclei play an important role at high temperatures.

The nuclear magnetization recovery traces of the ^{133}Cs nuclei were measured at several temperatures, and one of them is shown in Fig. 4(a) for the frequency domain, in which the central transition can be clearly resolved from the satellite transitions. The spin-lattice relaxation time, T_1 , was determined directly from the slope of the $\log [(S(\infty) - S(t))/S(\infty)]$ vs time t plot, as shown in Fig. 4(b).

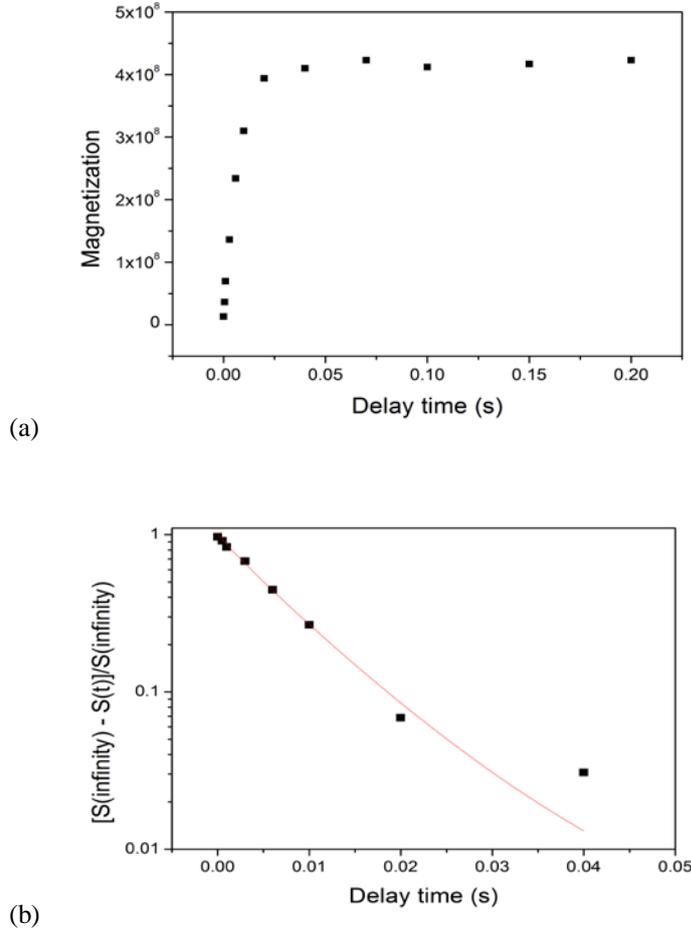


Figure. 4. (a) Magnetization recovery trace for ^{133}Cs in $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystals at room temperature and (b) the saturation recovery behavior of ^{133}Cs as a function of the delay time.

The recovery trace for the central line of ^{133}Cs can be represented by a combination of four exponential functions. The solid curve in Fig. 4(b) is the best fit to the data using Eq. (1). The temperature dependences of the ^{133}Cs spin-lattice transition rate W were fitted with Eq. (1) and the

^{133}Cs relaxation time was obtained in terms of W ($T_1=1/W$). The temperature dependence of the ^{133}Cs spin-lattice relaxation time, T_1 , for the $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals is shown in Fig. 5. The ^{133}Cs T_1 is nearly constant below 350 K and changes abruptly at the phase transition temperature 375 K ($=T_c$); at this temperature the ^{133}Cs NMR spectrum and DSC data have features consistent with a phase transition. The ^{133}Cs T_1 increases abruptly above 375 K, which reflects the transformation of the Cs^+ environment at the phase transition temperature.

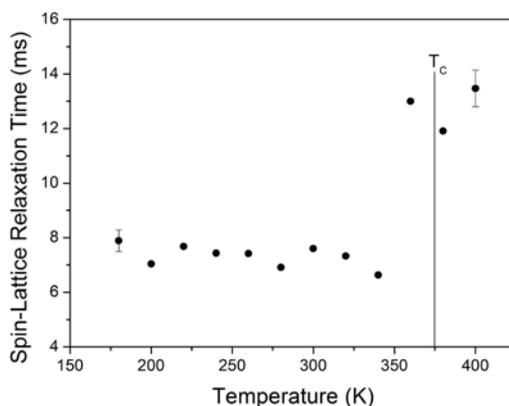


Figure. 5. Temperature dependence of the spin-lattice relaxation time T_1 for ^{133}Cs in a $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ single crystal.

DISCUSSION

The $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ crystals were grown using the slow evaporation method, and their lattice constants were confirmed with X-ray diffraction. The physical properties and phase transition temperature of this crystal were investigated with ^{133}Cs NMR relaxation analysis and DSC. The

presence of two types of Cs groups indicates that this crystal has the characteristics of a ferroelastic twin structure. The phase transition was found to take place at 375 K. The number of resonance lines in the ¹³³Cs spectrum changes from seven to one near T_C, which is due to a structural transformation; this change arises because the electric field gradient value becomes zero at T_C. These results suggest that the relaxation time of the ¹³³Cs nuclei undergoes significant changes near T_C. The observed changes in the temperature dependence of T₁ near T_C are thus related to variations in the symmetry of surrounding Cs⁺. The change in the temperature dependence of T₁ near T_C is related to the loss of H₂O and means that the forms of the octahedra of water molecules surrounding Cs⁺ are disrupted. The T₁ values of crystals containing paramagnetic ions are shorter than those of pure crystals; the influence of the paramagnetic ions is dominant. The relaxation time is expected to be inversely proportional to the square of the magnetic moment of the paramagnetic ions. Therefore, the relaxation times of materials containing Mn²⁺ ions are shorter than those of materials without paramagnetic ions. Mn²⁺ spin dynamics clearly dominate the spin-lattice relaxation behaviors of Mn-based compounds. A shorter T₁ indicates that the transfer of energy from the nuclear spin system to the surrounding environment is more easy. Therefore, the ¹³³Cs spin-lattice relaxation is driven by the fluctuations of the magnetic dipole of the Mn²⁺ paramagnetic ions.

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