

^{133}Cs NMR Spin-Lattice Relaxation Study in Incommensurate Cs_2CdI_4

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^{133}Cs NMR spin-lattice relaxation times (T_1) in crystalline Cs_2CdI_4 were measured at 225 - 373 K. The critical exponent ζ of T_1 observed near the normal-incommensurate transition in the normal phase was determined to be 0.62 ± 0.03 , in good agreement with the predicted value for three-dimensional XY -model. The frequency dependent T_1 in the incommensurate phase could be explained by the fluctuation of amplitudon and small gap phason.

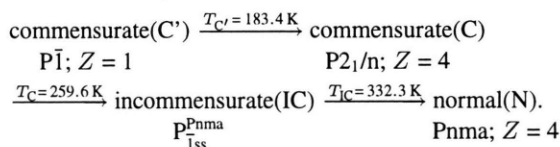
Key words: ^{133}Cs NMR; T_1 ; Incommensurate; Phase Transition; Critical Exponent.

Introduction

Many compounds of the A_2BX_4 family with a pseudo-hexagonal $\beta\text{-K}_2\text{SO}_4$ structure (Pnma) have been reported to have a normal (N) to incommensurate (IC) phase transition at low temperatures [1]. The critical behaviour of most of these compounds around the N-IC phase transition can be described by the XY -model [2]. In [3] we have reported results of ^{133}Cs NMR observed in Cs_2HgBr_4 crystals and found a critical exponent ζ of the spin-lattice relaxation rate that is different from the expected value from the XY -model but rather close to the classical value. In this compound, the dynamics of the IC phase modulation wave could also be described by the classical plane-wave-approximation in all temperature range of the IC phase [3]. In the present study, we selected Cs_2CdI_4 , reported to form an IC phase below 259.6 K [4], and intended to reveal the mechanism of the N-IC phase transition by comparing NMR results with those obtained for Cs_2CdBr_4 and Cs_2HgBr_4 [3].

Cs_2CdI_4 forms two modifications, A and B at room temperature, depending on the conditions of crystal growth. The modification A (orthorhombic Pnma) is obtained from a fused stoichiometric mixture of CsI and CdI_2 , while the monoclinic modification B ($\text{P2}_1/\text{m}$) crystallizes from the aqueous solution [5]. B undergoes no phase transition below room temperature but transforms to A at *ca.* 420 K. On the other

hand, A undergoes successive phase transitions [4]:



The N and C phases were shown to be isomorphous with corresponding phases in Cs_2HgBr_4 [6], while a modulation wave vector in the IC phase ($q_{\text{IC}} \simeq 0.26a^*$) [4] is different from that in the bromo compound ($q_{\text{IC}} \simeq 0.15a^*$) [7].

Experimental

Cs_2CdI_4 crystals were grown by slow evaporation of an aqueous solution containing stoichiometric amounts of CsI and CdI_2 . The obtained crystalline powder was kept *in vacuo* at 450 K to be transformed to the modification A, then sealed in a glass tube with nitrogen gas for differential thermal analysis (DTA) and NMR measurements.

X-Ray powder diffraction and DTA were measured to confirm the complete transformation to the modification-A. The sample temperature was determined by a chromel-constantan thermocouple within ± 0.2 K. The ^{133}Cs NMR measurement was performed with a Bruker MSL-300 NMR system at a Larmor frequency of 39.4 MHz in the range 225 - 373 K. The ^{133}Cs NMR T_1 in IC phase was measured by a Bruker

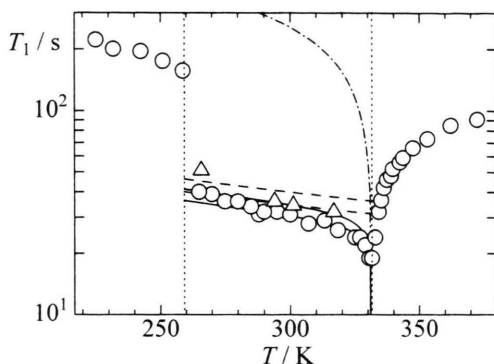


Fig. 1. Temperature and frequency dependences of ^{133}Cs NMR T_1 at 39.4 MHz ($\circ$) and 52.5 MHz (Δ). Solid lines are calculated values for the contributions from amplitudon (chain line) and phason (broken lines). The vertical dotted lines corresponds to phase transition temperatures observed by DTA measurement.

MSL-400 system at 52.5 MHz in the range 266 – 317 K. The sample temperature was controlled within ± 0.5 K by a Bruker VT-1000 temperature controller and determined by a copper-constantan thermocouple within ± 0.5 K. The error in T_1 was estimated to be 5%.

Electric charges on isolated HgBr_4^{2-} , CdBr_4^{2-} and CdI_4^{2-} were calculated by the semi-empirical method PM3 assuming a regular tetrahedral structure with the reported bond-length [8], without structural optimization.

Results

X-Ray Powder Diffraction and DTA

X-Ray powder diffraction peaks in neat crystals obtained from aqueous solution and after heat-treatment at 450 K were well explained by the reported structures [5, 9] of the modification B and A, respectively. In all following experiments, we used the heat-treated specimens.

DTA thermograms measured on heating displayed endothermic anomalies due to phase transitions at 183 ± 1 , 259.3 ± 0.6 and 331.6 ± 0.7 K, in good agreement with the reported transition temperatures, T_C , T_C and T_{IC} [4, 10, 11], respectively.

^{133}Cs NMR Spin-Lattice Relaxation Time T_1

The temperature dependence of ^{133}Cs T_1 is shown in Figure 1. The observed T_1 showed a sharp decrease

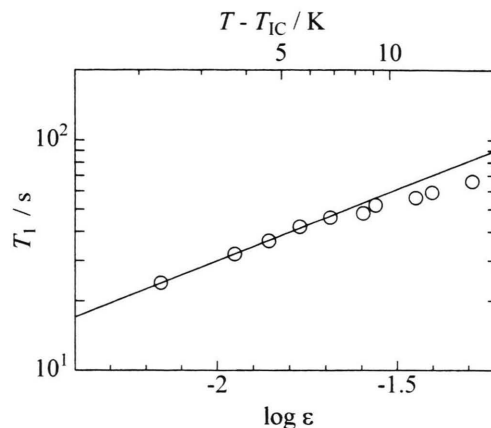


Fig. 2. A temperature dependence of critical ^{133}Cs NMR T_1 in the normal phase near the N-IC phase transition. The solid line represents calculated values for the critical exponent $\zeta = 0.62$.

and a jump near the N-IC and the IC-C phase transition point, respectively. T_1 revealed a weak frequency dependence, $T_1 \propto \omega^{0.45}$, on the high-temperature side of the IC phase.

Discussion

Normal (N) Phase

The T_1 dip observed near the phase transition temperature is attributable to the critical fluctuation of quadrupole interaction due to the second order phase transition. In this case, T_1 can be represented by the sum of two mechanisms as

$$T_1^{-1} = T_{lc}^{-1} + T_{ll}^{-1}, \quad (1)$$

where T_{lc} and T_{ll} are contributions from the critical fluctuation and non-critical lattice vibrations, respectively. Near the phase transition temperature, T_{lc}^{-1} shows an exponential divergence [12],

$$T_{lc}^{-1} \propto \epsilon^{-\zeta}, \quad (2)$$

where $\epsilon = (T - T_{IC})/T_{IC}$ and ζ are the reduced temperature and the critical exponent, respectively. $T_{ll} \geq 100$ s can be estimated from the observed T_1 at 370 K. ζ was obtained, from the slope of $\log T_1$ vs. $\log \epsilon$ plots, to be 0.62 ± 0.03 in a temperature range of 7 K above the transition (Figure 2). This

value coincides with that obtained in Cs_2CdBr_4 [3] and agrees well with the theoretical value of 0.625 [13] calculated for the three-dimensional XY -model with which the driving interaction of the N-IC phase transition is predicted [2]. The deviation of the observed T_1 values from the calculated ones at temperatures higher than 7 K above the phase transition is attributable to the contribution from T_{1l} .

Incommensurate (IC) Phase

The T_1 values in this phase, smaller than in the N and C phases, sharply decreased around the N-IC transition point. This behaviour is explainable by considering two characteristic lattice modes, amplitudon and phason, which represent the fluctuations of IC modulation [14]. The total T_1 is then represented by,

$$T_1^{-1} = T_{1l}^{-1} + T_{1a}^{-1} + T_{1\phi}^{-1}, \quad (3)$$

where T_{1a} and $T_{1\phi}$ are the contributions from the amplitudon and the phason, respectively. Since the T_1 values observed in the IC phase were one order shorter than those in the N and C phases (Fig. 1), the contribution from normal lattice modes T_{1l}^{-1} is assumed to be negligible.

In the plane wave limit, the contributions from amplitudon and phason are given by

$$T_{1a}^{-1} \propto (T_{1c} - T)^{-\zeta'}, \quad (4)$$

and

$$T_{1\phi}^{-2} \propto T^2 \left(\sqrt{1 + (\omega_L/\omega_\phi)^2} + 1 \right)^{-1}, \quad (5)$$

[15, 16], where ζ' is the critical exponent of T_1 on the low-temperature side of the phase transition point and ω_ϕ is the phason frequency or gap. In the frequency region $\omega_\phi \ll \omega_L$, the $T_{1\phi}$ is proportional to $\sqrt{\omega_L}$. The experimentally derived frequency dependence of T_1 in this phase, $T_1 \propto \omega^{0.45}$, approximately agrees with the predicted relation $T_1 \propto \sqrt{\omega_L}$. This implies that the phason gap is small enough compared with the Larmor frequency.

Based on the above discussion, we fitted the observed T_1 in the IC phase by a superposition of T_{1a} , and $T_{1\phi}$, as shown in Figure 1. In (4), we assumed the classical value $\zeta' = 0.5$ because the contribution

from the amplitudon was shown to emerge only in the neighbourhood of T_{1c} [3] and could not be separated from the total T_1 .

A small deviation of the calculated line from the observed T_1 in the low-temperature region of the IC phase is explainable by the breakdown of the plane-wave approximation for the IC modulation. This T_1 behaviour is analogous to the results obtained for Cs_2CdBr_4 [3].

Commensurate (C) Phase

In the C phase, ^{133}Cs T_1 is governed by normal lattice vibrations because the IC modulation wave is locked in a commensurate wave [1, 14]. The observed T_1 was longer than in the IC phase and the high-temperature region of the N phase, and showed a moderate dependence on temperature. No anomaly was observed near the first-order C-IC transition at 183 K.

Interionic Interaction and Transition Mechanism

In the present study we showed that the value of critical exponent of T_1 in the N-phase near the N-IC phase transition and T_1 behaviour in the IC phase are quite analogous to those in the previously reported Cs_2CdBr_4 [3]. We can reasonably expect that the interionic interaction between Cs cations and complex anions influences the critical dynamics near the phase transition and the behaviour of IC modulation wave. Here, we attempt to explain the relation of the dynamics around the transition and in the IC phase using interionic electrostatic interactions. The ionicity of halogen can be estimated from the observed e^2Qq/h using the Townes-Dailey relation [17]:

$$e^2Qq/h = (1 - s)(1 - i)(e^2Qq/h)_{\text{atom}}, \quad (6)$$

where s is the contribution of s electrons in the chemical bond and assumed to be 0.15, i is the ionicity of the halogen and $(e^2Qq/h)_{\text{atom}}$ is the e^2Qq/h of atomic halogen. The averaged electric charges per a halogen in the polyanions were calculated from (6) to be $-0.71 \sim -0.66$ for HgBr_4^{2-} , $-0.79 \sim -0.76$ for CdBr_4^{2-} and $-0.74 \sim -0.71$ for CdI_4^{2-} from the reported NQR frequencies [6, 18] observed near room temperature by assuming $\eta = 0$. The ionicities of isolated polyanions, obtained by PM3 calculations,

were -0.676 for HgBr_4^{2-} , -0.836 for CdBr_4^{2-} and -0.835 for CdI_4^{2-} . The NQR frequencies and PM3 calculations yield quite analogous results: CdBr_4^{2-} and CdI_4^{2-} are more ionic than HgBr_4^{2-} . This difference of the halogen ionicity seems to induce the different behaviour, *i.e.*, the XY -interaction near the N-IC transition and the multi-soliton IC-modulation work in Cs_2CdI_4 and Cs_2CdBr_4 crystals, whereas the classical behaviour prevails in Cs_2HgBr_4 crystals.

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