NQR Parameters in Incommensurate Cs_2CdBr_4 and Cs_2HgBr_4 Crystals *

Hirokazu Nakayama, Nobuo Nakamura, and Hideaki Chihara
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560, Japan

The temperature dependence of the [81]Br spin-lattice relaxation times for Cs_2CdBr_4 and Cs_2HgBr_4 was measured in the low temperature and the commensurate phases. For the commensurate phase of Cs_2CdBr_4 rapid shortening of the T_1 of $v_B \sim v_C$ was observed on approaching the "lock-in" transition point. It is probably due to an anisotropic critical fluctuation. On the other hand, T_1 in the low temperature phase of Cs_2HgBr_4 behaves like an order parameter but no critical decrease of T_1 was observed in the commensurate phase.

Introduction

A number of A_2BX_4 type crystals having β-K_2SO_4 structure (Pnma, $Z = 4$) show successive phase transitions. Some compounds possess incommensurate (IC) phases and have recently attracted great attention; among them Rb_2ZnBr_4, Rb_2ZnCl_4, and K_2SeO_4 have been studied by a variety of experimental methods.

Cs_2CdBr_4 [1] and Cs_2HgBr_4 [2] are isomorphous to these compounds. On cooling, they undergo a phase transition to an IC phase at 252 K [3, 4] and 243 K [2, 3], respectively. The IC phase assumes a modulated structure by an IC wave propagating along the crystallographic a-axis with $q = 0.15\,a*$ [3]. On further cooling the transition $IC \to C$, i.e., the "lock-in" transition occurs at 237 K for Cs_2CdBr_4 and at 232 K for Cs_2HgBr_4; it leads to $q = 0$. A low temperature phase appears below 156 K for Cs_2CdBr_4 and below 165 K for Cs_2HgBr_4. The fact that the line at the lowest frequency splits into two when the crystal is cooled down to the C phase suggests that the normal and the C phases are related with each other by the Γ_4^+ mode [3], which represents the rotation of the tetrahedral anions about the a-axis. Therefore a small angle rotation or tilt of the anions about the a-axis may play an important role in the successive phase transitions.

We have made a model calculation of the electric field gradient at each bromine site in the normal, the IC, and the C phases and confirmed that the IC modulation wave consists of a successive rotation or tilt of the anions about the a-axis, and we found that the NQR linewidths of v_2 and v_3 (in the normal phase) become too broad to be detected in the IC phase [5]. This paper reports on measurements of the [81]Br spin-lattice relaxation time T_1 for Cs_2CdBr_4 and Cs_2HgBr_4 in order to understand the mechanism of the successive phase transitions from the dynamical point of view.

Experimental

Crystalline Cs_2HgBr_4 [6] and Cs_2CdBr_4 [7] were synthesized from stoichiometric mixtures of CsBr and MBr_2 (M=Hg, Cd) by the Bridgeman method. The samples obtained were ground and sealed in glass ampoules with helium gas of about 60 Torr for the NQR measurements.

[81]Br NQR was observed with a MATEC pulsed spectrometer. The matching unit was placed into the cryostat in order to attain impedance matching easily. Since the temperature coefficient of the NQR frequencies was large, the temperature of the sample was controlled to within ± 0.05 K during each run. Accumulation of FID was made prior to the T_1 measurements with a transient recorder. The spin-lattice relaxation time was measured by the $180° - \tau - 90°$ method to within the error of 10%. Recovery of the magnetization was always represented by a single exponential function of time.

The temperature was measured with chromel P-constantan thermocouples. Details of the spectrometer and its operation were described elsewhere [8].

Results and Discussion

(1) Cs_2CdBr_4

Two groups of researchers [3, 9] reported different transition temperatures for this compound. Although the reason for this difference is not clear, our transition temperatures agree with those found by Plesko et al. [3] within ± 2 K. The temperature dependence of the NQR frequencies is shown in Figure 1 a. The spin-lattice relaxation times in the C-phase and the low temperature phase are shown in Figure 2. The numbers in these figures correspond to the line numbers in Figure 1 a. The spin-lattice relaxation times for the other lines (5–8) are almost the same as those in Figure 2 b. The spin-lattice relaxation times in the normal phase could not be measured because the T_1's were very short ($\sim 100\,\mu s$) in this phase. The figures show several characteristic features. Near the low temperature − C phase transition point no anomalous behavior of T_1 was observed. For the line A (and the lines 1 and 2 in the low temperature phase) T_1 obeys a T^2 law [10] in the whole temperature range, indicating that the relaxation is governed by a librational motion of the $[CdBr_4]^{2-}$ tetrahedra. On the other hand, for the lines B and C the T_1's vary as T^2 up to about 200 K, and then a steep decrease of T_1 is observed on approaching the "lock-in" phase transition point. Such a rapid shortening of T_1 of only the $v_B \sim v_C$ lines may be attributed to a critical slowing down of the cooperative librational motion of the $[CdBr_4]^{2-}$ tetrahedra about the crystallographic a-axis, which is nearly parallel to the Cd−Br (1) bond axis. Although the lock-in transition is of first order and a theoretical treatment of the $C-IC$ transition did not predict any critical fluctuation at the lock-in transition point, it is not unreasonable to consider the existence of some rotational critical fluctuation because the rotation about the a-axis may continuously work through the C, IC and the normal phases in this substance [3].

(2) Cs_2HgBr_4

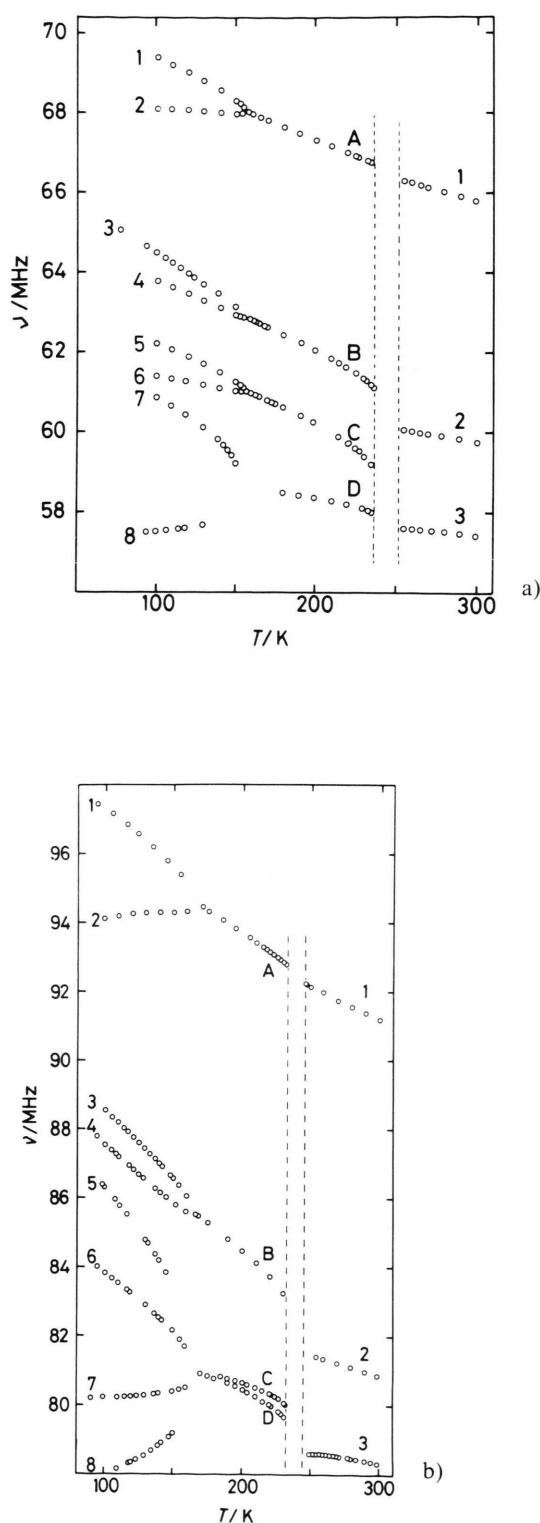The transition temperatures found by us agree with those reported by Plesko et al. [3] within

Fig. 1. Temperature dependence of [81]Br NQR frequencies (a) in Cs_2CdBr_4, and (b) in Cs_2HgBr_4.
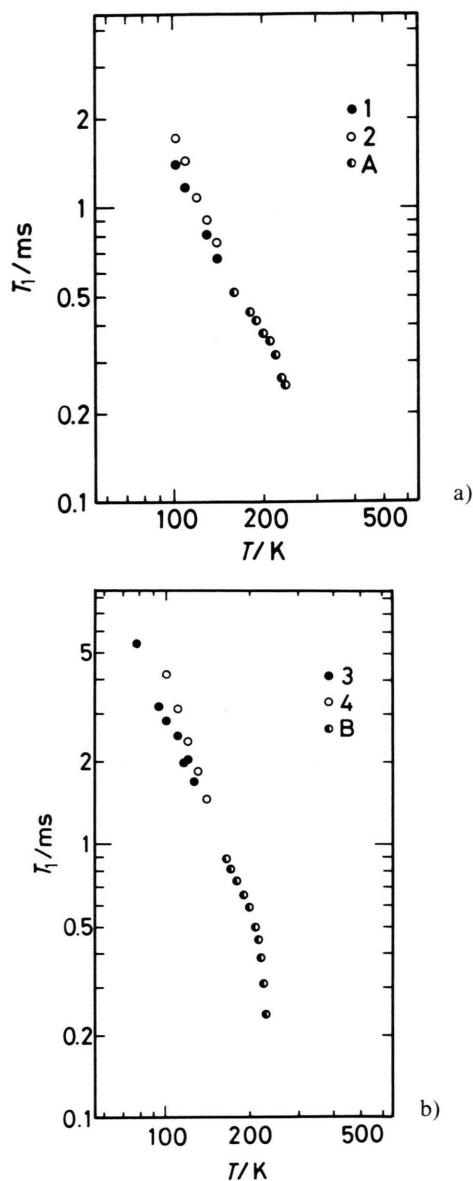
Fig. 2. Temperature dependence of ^{81}Br NQR spin-lattice relaxation times in Cs$_2$CdBr$_4$. The numbers correspond to the numbers in Figure 1 a.
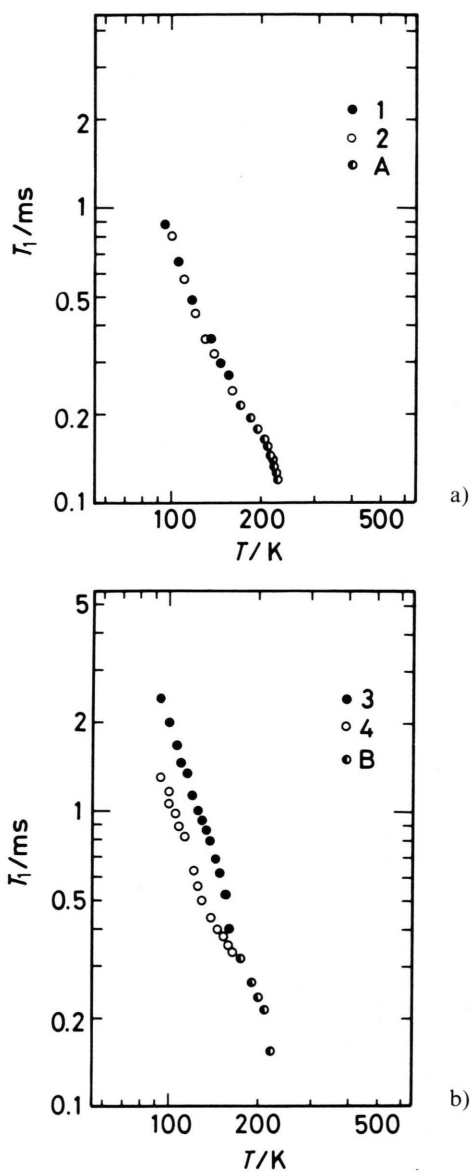

Fig. 3. Temperature dependence of ^{81}Br NQR spin-lattice relaxation times in Cs$_2$HgBr$_4$. The numbers correspond to the numbers in Figure 1 b.

± 2 K. The temperature dependence of the NQR frequencies is shown in Figure 1 b. The T_1's in the C and the low temperature phase are shown in Figure 3. The numbers in these figures correspond to the line numbers in Figure 1 b. No critical fluctuation near the "lock-in" transition was observed, contrary to the case of Cs$_2$CdBr$_4$. The absolute values of the frequencies are larger than those in Cs$_2$CdBr$_4$ by a factor of about 10/7, so that T_1 for Cs$_2$HgBr$_4$ is shorter than that for Cs$_2$CdBr$_4$ and the possible critical fluctuation was obscured by the very effective non-critical librational motion of [HgBr$_4$]$^{2-}$.

The T_1's of the v_3 and v_4 lines show an interesting behavior. On approaching the C−low temperature phase transition point the difference between their T_1's becomes smaller like the order parameter of a second order phase transition. Yet there have not been found any compounds in which the T_1's behave like an order parameter of phase transition. This may be closely related to the mechanism of the phase transition.

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