^{81}Br Nuclear Quadrupole Resonance of Cs_2ZnBr_4 and Crystal Stability of Compounds of A_2MX_4 Type

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(Received July 16, 1986)

The temperature dependences of ^{81}Br nuclear quadrupole resonance frequencies and quadrupolar relaxation times of Cs_2ZnBr_4 were measured. The librational motion of $[ZnBr_4]^{2-}$ about the Zn–Br axis parallel to the a axis in the crystal is more active than those about the other axes. The reason why this compound shows no phase transition can be accounted for by the molecular packing, especially the packing of $[ZnBr_4]^{2-}$ along the a axis. General examination of the relative size of cation/anion in the class of compounds of A_2MX_4 type led to a criterion which may be used to rationalize existence and absence of a phase transition.

A large number of A_2MX_4 type of compounds crystallize in the isomorphous structure with the space group *Pnma* and undergo analogous sequence of phase transitions. Among them much attention has recently been focused on Rb_2ZnBr_4 and Rb_2ZnCl_4 from experimental and theoretical points of view because they assume typical incommensurate structure in certain temperature regions. Cs_2HgBr_4[1)] and Cs_2CdBr_4[2)] also belong to this group and have interested us as they[3–6)] show similar successive phase transitions from the normal room temperature phase to the phase of incommensurate structure and then to the commensurate phase on further cooling. We studied the microscopic structure of the incommensurate phases of these latter two materials by relating the nuclear quadrupole resonance results with a model calculation of the electric field gradients at the bromine sites.[7)]

Cs_2ZnBr_4 also has the A_2MX_4 composition and crystallizes in the *Pnma* structure.[8)] However no phase transition has been found in this compound so far.[3)] These facts suggest that the structural stability of this type of compounds depends on a very intricate balance of interatomic forces and that the phase transition phenomena have to occur when such an intricate balance is destroyed. Hence it will be of great interest to uncover a factor or factors which govern the crystal stability and the cooperative phase change phenomena of such series of materials.

This paper is aimed first at deducing some information about the feature of the molecular motion in Cs_2ZnBr_4 from the temperature dependence of nuclear quadrupole resonance frequencies and spin-lattice relaxation times. The second purpose is to pin down the physical properties that determine the crystal structure and trigger the phase transition of these materials.

Experimental

Crystalline Cs_2ZnBr_4[8)] was obtained by slow evaporation of aqueous solution of the stoichiometric amounts of CsBr and $ZnBr_2$ at room temperature. The sample was recrystallized twice from aqueous solution, ground and sealed in an ampule with helium gas for the NQR measurements.

The ^{81}Br NQR signal was observed with a home-built pulsed FT spectrometer based on a MATEC spectrometer. The matching unit was placed in the cryostat in order to make impedance matching easy. Details of the apparatus and its operation were reported elsewhere.[9)]

The temperature dependence was determined by using a simple cryostat with liquid nitrogen as the refrigerant. The temperature, kept constant to within ±0.1 K during the NQR measurements, was measured with Chromel P-Constantan thermocouples.

Results and Discussion

Cs_2ZnBr_4. The temperature dependence of the nuclear quadrupole resonance frequencies is shown in Fig. 1. There are three resonance lines in the temperature range between 77 and 300 K in accordance with the X-ray structure data.[8)] Our frequency data agree with those by Plesko et al.[3)] within 100 kHz in the temperature range measured. We may assign the three resonance lines ν_1, ν_2, and ν_3 to the bromine 1, 2, and 3 in the structure data[8)] respectively by reference to the NQR data of the isomorphous Cs_2CdBr_4.[6)] One sees from this figure that the temperature coefficient of the resonance line at the site 1 is only $-2\,\mathrm{kHz\,K^{-1}}$ in comparison with -6.5 kHz for the line at the site 2, indicating that the librational motion of the $[ZnBr_4]^{2-}$ tetrahedron is highly anisotropic. Since the direction of the bond between the bromine at the site 1 and the central metal almost coincides with the crystallographic a-axis, the above fact means that only the libration of the anion about the a-axis is highly excited. This interpretation is also supported by the relaxation time measurements. The temperature dependence of the ^{81}Br spin-lattice relaxation time, T_1, is shown in Fig. 2. The relaxation rate, T_1^{-1}, obeys the T^2 law[10)] for all the

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lines between 77 and 300 K, indicating that the relaxation of the bromine nuclei at all the sites is governed by the librational motion of the $[ZnBr_4]^{2-}$ tetrahedron. According to the theory of the quadrupolar relaxation[10] due to vibration,

$$T_1^{-1}(\nu_1) : T_1^{-1}(\nu_2) : T_1^{-1}(\nu_3) = \nu_1^2 : \nu_2^2 : \nu_3^2$$

holds if the molecular or the ionic motion is isotropic. Hence, the relaxation time of the ν_1 line would be the shortest if the isotropic anionic librations were excited. The experimental T_1 of the ν_1 is, however, more than twice as long as those of the other two lines, which supports again that the libration about the a-axis, which does not essentially affect the T_1 for ν_1, is sufficiently excited but those about the other axes have only small amplitudes.

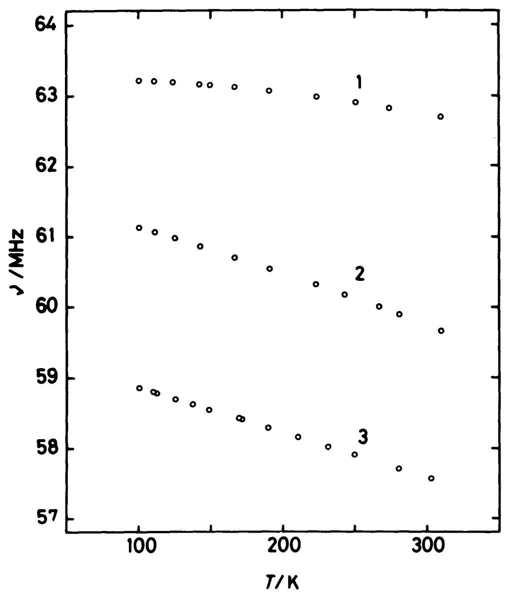

Fig. 1. Temperature dependence of ^{81}Br NQR frequencies in Cs_2ZnBr_4.

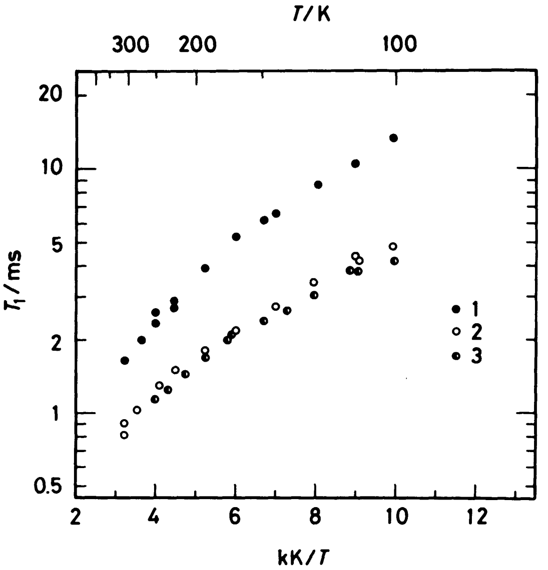

Fig. 2. Temperature dependence of ^{81}Br NQR spin-lattice relaxation times in Cs_2ZnBr_4.

In a previous paper[7] we showed that in Cs_2MBr_4 (M=Hg, Cd) the librational motion of the $[MBr_4]^{2-}$ (M=Cd, Hg) tetrahedron about the a-axis is highly excited in their normal phases and that such anisotropic libration is responsible for the phase transition to the incommensurate phase in which the rotational displacement of the anions about the a-axis generates the incommensurate wave along the a-axis.

Thus, we see that the compounds Cs_2MBr_4 (M=Hg, Cd) and Cs_2ZnBr_4 have a common feature; i.e., the librational mode is highly excited about the a-axis in the *Pnma* phase of each substance and it may be the cause of existence or non-existence of successive phase transitions in these isomorphous substances.

Phase Relation and Stability of A_2MX_4 Structure. The compounds Cs_2CdBr_4[3,5,6] and Cs_2HgBr_4[1,3–5] show successive phase transitions and become incommensurate in a certain temperature region. Their structures and phase transitions such as the transition temperature, the length and distance of the incommensurate wave vectors and the phase relation below T_c, etc., are very similar to each other. On the other hand, Cs_2ZnBr_4[3] shows no phase transition although its crystal structure[8] at room temperature is isomorphous to Cs_2HgBr_4[1] and Cs_2CdBr_4,[2] and these three compounds show common characteristic as mentioned in the preceding section. In an attempt to uncover a factor or factors which govern the phase relations and the stability of the *Pnma* structure, a comparison will be made of the structural characteristics of a variety of A_2MX_4 type compounds.

The space group of the highest temperature phase of each of A_2MX_4 type compounds (A=K, Na, Rb, Cs; B=Hg, Cd, Zn, Co, Mn, Cu; X=Cl, Br, I)[1,2,8,11–25] is listed in Table 1. From this table two interesting

Table 1. Space Group of A_2MX_4 Type of Compounds

Complex anion	Cation			
	Na	K	Rb	Cs
$HgCl_4$				*Pnma*[11]
$HgBr_4$				*Pnma*[1]
HgI_4				$P2_1$[12]
$CdCl_4$	*Pbam*[13]			$I4/mmm$[14]
$CdBr_4$				*Pnma*[2]
CdI_4				
$ZnCl_4$	*Pnma*[15]	*Pnma*[16]	*Pnma*[17]	*Pnma*[18]
$ZnBr_4$			*Pnma*[19]	*Pnma*[3]
ZnI_4			$P2_1/m$[20]	*Pnma*[21]
$CoCl_4$	*Pnma*[15]	*Pnma*[22]	*Pnma*[23]	*Pnma*[24]
$CoBr_4$		*Pnma*[25] $P2_1/m$[20]	*Pnma*[25]	*Pnma*[25]
CoI_4		$P2_1/m$[22]	$P2_1/m$[22]	*Pnma*[22]

properties can be extracted.

1) The compounds that have the common cation and the anion of almost the same size crystallize in the same space group irrespective of the chemical species of metallic element. A_2CoX_4 and A_2ZnX_4 have the same space group when A and X are common. Thus the space group of both Cs_2CoCl_4 and Cs_2ZnCl_4 is *Pnma* and the space group of Rb_2CoI_4 and Rb_2ZnI_4 is $P2_1/m$. Moreover, the lattice constants in A_2CoX_4 and A_2ZnX_4 are almost the same as shown in Table 2. The same relation can be seen between A_2HgBr_4 and A_2CdBr_4.

Table 2. Space Group and Lattice Parameters of A_2ZnX_4 and A_2CoX_4

Compound	Space group	Lattice constant		
		a/Å	*b*/Å	*c*/Å
Na_2ZnCl_4	*Pnma*[15]	8.053	6.402	13.695
Na_2CoCl_4	*Pnma*[15]	8.073	6.428	13.713
K_2ZnCl_4	*Pnma*[16]	8.926	7.256	12.402
K_2CoCl_4	*Pnma*[22]	8.933	7.240	12.421
Rb_2ZnCl_4	*Pmcn*[17]	7.282	12.726	9.257
Rb_2CoCl_4	*Pmcn*[23]	7.283	12.723	9.272
Cs_2ZnCl_4	*Pnma*[18]	9.758	7.400	12.970
Cs_2CoCl_4	*Pnma*[24]	9.737	7.392	12.972
Rb_2ZnBr_4	*Pmcn*[19]	7.656	13.343	9.708
Rb_2CoBr_4	*Pmcn*[25]	7.651	13.371	9.718
Cs_2ZnBr_4	*Pnma*[3]	10.196	7.770	13.517
Cs_2CoBr_4	*Pnma*[25]	10.181	7.723	13.492
Rb_2ZnI_4	$P2_1/m$[20]			
Rb_2CoI_4	$P2_1/m$[22]	10.383	8.144	7.657
Cs_2ZnI_4	*Pmcn*[21]	8.29	14.45	10.84
Cs_2CoI_4	*Pmcn*[22]	8.297	14.414	10.833

Table 3. Existence of Phase Transition or Transitions in A_2MX_4 Compounds

Complex anion	Cation			
	Na	K	Rb	Cs
$HgCl_4$				YES[26]
$HgBr_4$				YES[1,4,7]
HgI_4				
$CdCl_4$				
$CdBr_4$				YES[4,5]
CdI_4				
$ZnCl_4$	?	YES[28]	YES[28]	NO[29]
$ZnBr_4$			YES[28]	NO[4]
ZnI_4				YES[30]
$CoCl_4$	?	?	?	NO[31]
$CoBr_4$		?	?	?
CoI_4		?	?	?

2) The relative size of the cation and the complex anion governs the space group of the highest temperature phase. Those are the properties that

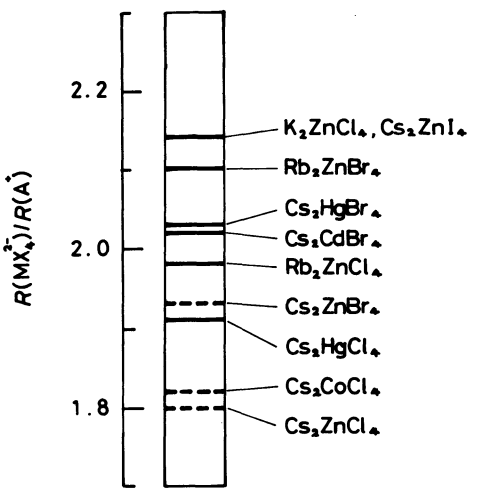

Fig. 3. Ratio of the effective radius of the complex anion $[MX_4]^{2-}$ to the radius of cation A^+ for various compounds.

——: Indicates a compound which has one or more phase transitions.

- - -: Indicates a compound which has no phase transition.

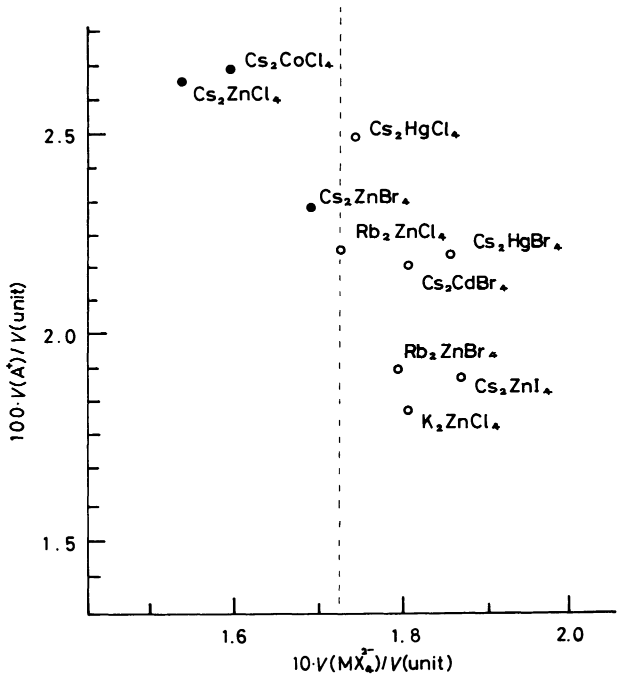

Fig. 4. The effective volume of the complex anion $[MX_4]^{2-}$ is plotted against the volume of the cation A^+ both reduced by the volume of the unit cell.

●: Indicates a compound which has phase transitions.

○: Indicates a compound which has no phase transition.

determine not only the crystal structure but also the phase relation. Table 3[1,3–6,26–31)] suggests that the key factor for the highest temperature phase to undergo a phase transition into an incommensurate phase is the relative size of the cation and the complex anion. In order to show that it is the key factor in a more quantitative manner, the relative sizes of the cation and the anion were calculated for each of these compounds and the result is shown in Fig. 3. The ionic radii of the cations were taken from reference 32 as 1.52 Å for K^+, 1.66 Å for Rb^+ and 1.81 Å for Cs^+. The ionic radii of $[MX_4]^{2-}$ complex anions were obtained by adding interatomic distance of M–X and the atomic radius of the X atom. The ratios between the ionic radii, $R([MX_4]^{2-})/R(A^+)$, calculated from these data are arranged in Fig. 3, where the solid lines represent compounds which undergo a phase transition or transitions and the broken lines those without any transition. This graph shows that the compounds with the ratio value between 1.9 and 2.2 show a phase transition except for slight displacement of Cs_2ZnBr_4. If, on the other hand, the volume occupied by a cation is plotted against the volume occupied by a complex anion, both reduced by the unit cell volume (Fig. 4), the compounds for which $V([MX_4]^{2-})/V(\text{unit cell})$ is larger than 0.172 undergo at least one phase transition almost independent of the value of $V(A^+)/V(\text{unit cell})$. It thus seems that $V([MX_4]^{2-})/V(\text{unit cell})=0.172$ is the critical value for A_2MX_4 type compounds; it serves as a gross criterion for distinguishing whether a compound with A_2MX_4 type structure undergoes any phase transition or not.

We saw in the preceding section that the anisotropic interaction plays an important role in the phase transition phenomena in the A_2MX_4 type of substances. In order to search for an anisotropic property

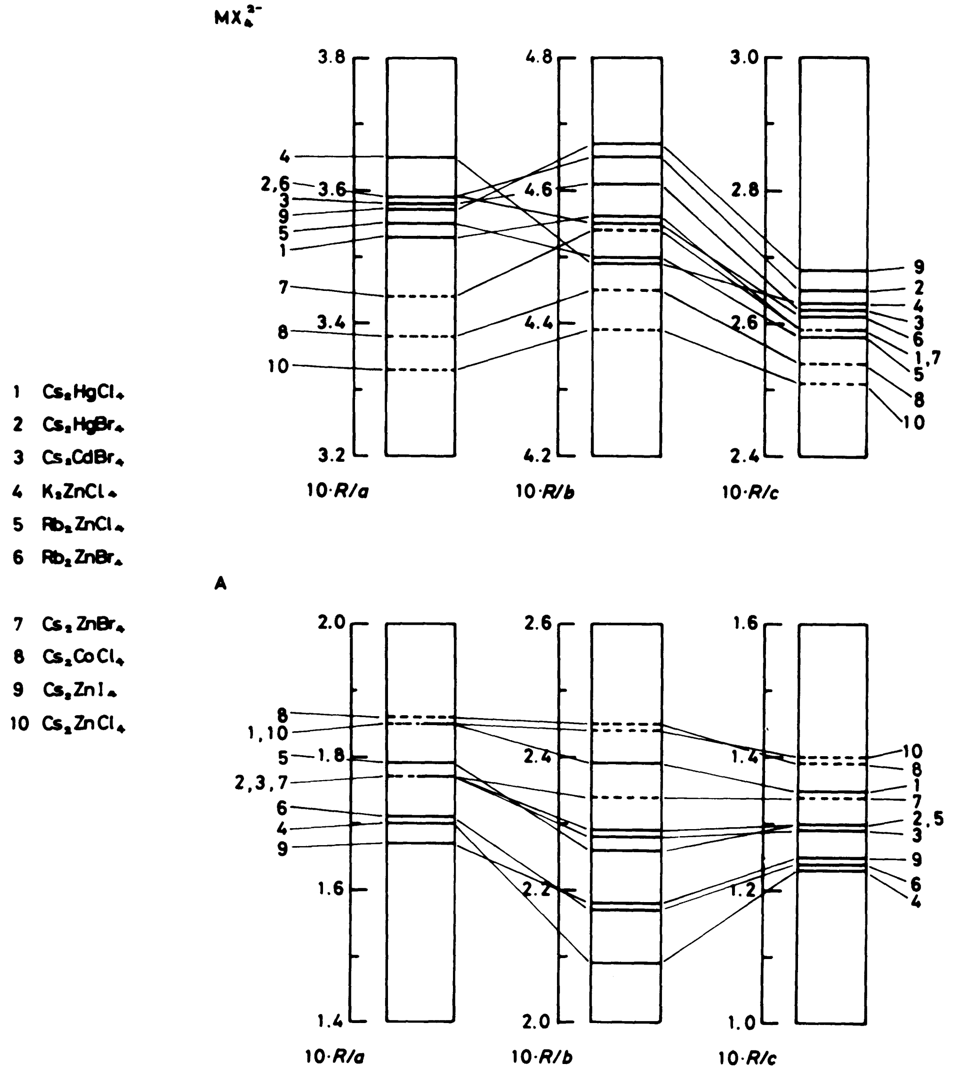

Fig. 5. Ratio of the radius of the complex anion $[MX_4]^{2-}$ and that of the cation A^+ to the individual lattice constants in various compounds are shown in the upper and the lower figures, respectively. ---: Indicates a compound which has no phase transition.

governing the crystal stability, we arranged the ionic radius $R(A^+)$ or $R([MX_4]^{2-})$ reduced by each of the lattice constants in the order of their magnitude as shown in Fig. 5. The compounds with and without any phase transition are highlighted by the solid and broken lines, respectively. These diagrams suggest that the compounds composed of a small cation and a large complex anion undergo a phase change. Especially, this tendency is distinct in regard to the quantity $R([MX_4]^{2-})/a$, i.e. the compounds with this ratio greater than 0.35 undergo some kind of phase transition. This finding is very important in that the compounds which possess an incommensurate phase show the incommensurate wave vector directed in the a-axis. Even the compounds that do not have an incommensurate phase show tripled unit cell in the a axis direction in the low temperature phase. We can therefore state that the ionic interaction along the a-axis mainly govern the stability of a particular crystal structure with regard to incommensurate modulation.

In this way we can interpret the fact that both Cs_2HgBr_4 and Cs_2CdBr_4 undergo successive phase transitions while the isomorphous Cs_2ZnBr_4 doesn't exhibit any phase transition: The anisotropic interaction along the crystallographic a-axis in Cs_2ZnBr_4 is small whereas in the former two compounds a strong cooperative interaction exists along the a-axis and may drive these materials to undergoing phase transitions on cooling.

We can now use our finding to predict the phase transition of the A_2MX_4 type of materials, i.e., a compound of A_2MX_4 type in which the value of $R([MX_4]^{2-})/a$ is slightly smaller than 0.35 is a candidate which undergoes a phase transition at high pressure because external pressure will increase this ratio up to 0.35 and then the original structure may become less stable.

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