^{79}Br and ^{127}I Nuclear Quadrupole Resonance of Mixed Valency Compounds Ga_2X_4(X=Br, I)

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Synopsis. ^{79}Br and ^{127}I nuclear quadrupole resonances(NQR) were observed in α-Ga_2Br_4, β-Ga_2Br_4, and Ga_2I_4 at various temperatures. Resonance lines disappeared at 353, 335, and 448 K for α-, β-Ga_2Br_4, and Ga_2I_4 respectively. The wide separation of the ^{127}I resonance lines in Ga_2I_4 may be attributed to the interaction between the Ga^+ ions and the I atoms.

The X-ray crystal analysis has shown that Ga_2Cl_4 is a mixed valency compound with the ionic structure of $Ga^+(GaCl_4)^-$, that the Ga atom is tetrahedrally coordinated by four Cl atoms, and that the Ga^+ ion is surrounded by eight Cl atoms.[1] The Raman spectrum has revealed that Ga_2Br_4 fused at about 453 K also has the ionic structure of $Ga^+(GaBr_4)^-$.[2] Corbett and Hershaft have reported that Ga_2Br_4 exists in two crystalline forms, with melting points of 426 and 437.5 K.[3] Recently, X-ray crystal analysis has shown that Ga_2I_4 has an ionic structure similar to Ga_2Cl_4.[4]

In the present study, we observed the NQR of Ga_2X_4(X=Br, I) and examined the phase transitions and interionic interaction. The NQR of α-Ga_2Br_4 has already been investigated by Deeg and Weiss.[5]

Experimental

Ga_2Br_4 was prepared by heating equimolar amounts of Ga and $HgBr_2$ in a glass reaction tube.[6] The α-form was obtained by gradually cooling the mixture from 426 K, and the β-form, by cooling it rapidly from 438 K. Ga_2I_4 was prepared by heating equimolar amounts of Ga anf HgI_2 at 484 K in a glass tube. In each case, the compound was purified by eliminating Hg as a by-product.

NQR was measured by using superregenerative oscillators with Zeeman modulation. The temperature of the sample was determined with the aid of a copper-constantan thermocouple.

Results and Discussion

Table 1 shows the observed NQR frequencies of Ga_2X_4(X=Br, I). The ^{79}Br resonance frequencies of α-Ga_2Br_4 are in good agreement with those reported by Deeg and Weiss.[5] Two ^{79}Br resonance lines were also observed for β-Ga_2Br_4. The two lines of the β-form are widely separated, whereas those of the α-form are close to each other. The wide separation of the resonance lines suggests that the shape of the $GaBr_4^-$ ion is a distorted tetrahedron. In the case of Ga_2Cl_4, a contraction in volume has been reported by Fedrov and Lovetskaya when the α-form is transformed to the β-form.[7] This causes the intermolecular distances to shorten. Therefore, the influence of the crystal field on the electric field gradients becomes large, and the resonance lines result in a wide separation or multiple split. A similar relation can be expected to hold for Ga_2Br_4.

As the temperature was raised from 77 K, all the resonance lines in α- and β-Ga_2Br_4 decreased gradually in frequency, but the curves of the frequency *vs.* the temperature in the α-form crossed at about room temperature. The resonance lines disappeared at 353 and 335 K for the α- and β-forms respectively. When the temperature of each sample was brought back from the temperature of the line-disappearance to room temperature, however, no resonance lines could be observed. However, when each sample was once melted and then cooled to room temperature, its resonance lines could again be observed. Our differential thermal analysis measurements showed that, with an increase in the temperature from room temperature, one peak was recorded near 370 K for the α-form and two peaks were recorded near 355 and 390 K for the β-form.

TABLE 1. NQR PARAMETERS IN Ga_2X_4(X=Br, I) AT 293 K

Compound	Nucleus	Frequency/MHz[a]		η/%	$\frac{e^2Qq/h}{\text{MHz}}$
		$\nu_1(\pm1/2\leftrightarrow\pm3/2)$	$\nu_2(\pm3/2\leftrightarrow\pm5/2)$		
α-Ga_2Br_4	^{79}Br	128.85	—	—	—
	^{79}Br	128.92	—	—	—
β-Ga_2Br_4	^{79}Br	128.44	—	—	—
	^{79}Br	122.59	—	—	—
Ga_2I_4	^{127}I	113.65	227.09	2.62	757.08
	^{127}I	131.94	262.14	7.16	874.71
	^{127}I	134.27	262.61	13.24	878.46
	^{127}I	163.71	280.90	36.64	960.13

a) The experimental errors are within ±0.02 MHz for ^{79}Br and ^{127}I.

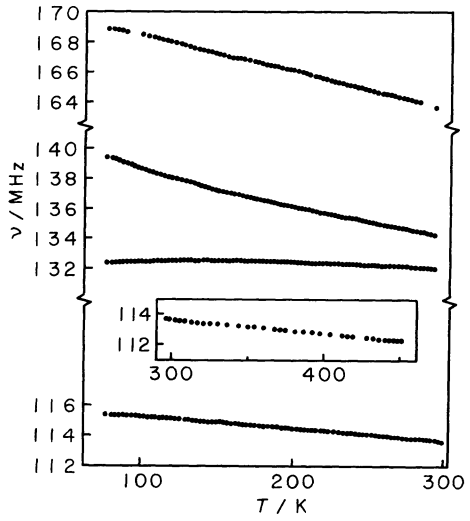

Fig. 1. Temperature dependence of ν_1 NQR frequencies of ^{127}I in Ga_2I_4.

Therefore, it seems likely that the disappearance of the resonance lines is due to the phase transition.

The eight ^{127}I resonance lines listed in Table 1 were observed for Ga_2I_4. There is an ambiguity in pairing the ^{127}I resonance lines because the pairing of these lines was done in the order of frequency. The other combination gives slightly different values for the asymmetry parameter, η, and the quadrupole coupling constant, e^2Qq/h. The four $\nu_1(\pm1/2\leftrightarrow\pm3/2)$ lines of ^{127}I are so widely separated that the small distortion in the shape of the GaI_4^- ion can not be attributed to the line separation.

According to the X-ray analysis by Gerlach *et al.*,[3] the Ga–I bond lengths are 2.537(5), 2.541(4), 2.541(4), and 2.608(4)Å, and all I–Ga–I angles are within 3.1° of the tetrahedral angle. The shape of the GaI_4^- ion slightly distorted from a regular tetrahedron; therefore, the distortion of the shape of the anion can not be reasonable as the cause of the line separation. The I···I distances in the GaI_4^- ion range from 4.121 to 4.266 Å, and the I···I distances between GaI_4^- ions are equal to the sum of the van der Waals radii.[3] Accordingly, the I···I distances can not cause the resonance lines to separate widely. One Ga^+ ion is surrounded by eight I atoms at distances ranging from 3.281 to 3.820 Å, and the number of Ga^+ ions with which a given I atom interacts differs with each crystallographically nonequivalent I atom.[3] Therefore, the wide separation of the resonance lines is ascribable mainly to the Ga^+···I interaction.

Figure 1 shows the temperature dependence of the ν_1 NQR frequencies of ^{127}I in Ga_2I_4. All the resonance lines decreased in frequency with the increase in the temperature. The slopes of the curve for the higher two resonance lines are large, while those of the rest are small. In the temperature region above room temperature, the temperature dependence was observed only for the lowest resonance line, as is shown in Fig. 1. As the temperature was raised, the resonance line decreased monotonously in its frequency. The intensity of the resonance line became gradually small from about 400 K and disappeared at 451 K. When the temperature was brought back to room temperature, the resonance lines could be observed again.

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