Temperature Dependences of ^{69}Ga and ^{81}Br NQR Frequencies in $[R_4N]_2Ga_2Br_6$ ($R=CH_3$ and C_2H_5)

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Synopsis. Temperature dependences of ^{69}Ga and ^{81}Br NQR frequencies showed that phase transitions take place at 98 and 137 K in $[(CH_3)_4N]_2Ga_2Br_6$ and that the C_3 reorientation of the $GaBr_3$ group occurs in $[(C_2H_5)_4N]_2Ga_2Br_6$ around room temperature.

Unusual temperature dependences of ^{69}Ga and ^{81}Br nuclear quadrupole resonance (NQR) frequencies were observed for $[R_4N]_2Ga_2Br_6$ ($R=CH_3$ and C_2H_5) in a study of bond character in Ga(II) compounds.[1] Although no crystal structure analysis of these two compounds has been reported as yet, we expect that the ethane-like $Ga_2Br_6^{2-}$ ions exist in both crystals, and that the cations are situated on the extension of the Ga-Ga bond of the $Ga_2Br_6^{2-}$ ion in a similar manner to the crystal of $[(CH_3)_4N]_2Ga_2Cl_6$.[2] On the basis of these expected crystal structures, we examined a possibility that unusual temperature dependences of ^{69}Ga and ^{81}Br NQR frequencies can be attributed to reorientations of the cation and/or anion.

Experimental

The compounds were prepared according to Ref. 3. NQR spectra of ^{81}Br and ^{69}Ga were recorded on a pen-recorder using a superregenerative oscillator with Zeeman modulation. The temperature dependence of the NQR frequencies was measured in the temperature range between 77 and ca. 300 K by immersing the sample into a bath of cooled petroleum-ether or heated silicone oil. The sample-temperature was measured using a copper-constantan thermocouple whose e.m.f. was displayed on a digital multimeter. Broad-line ^1H NMR spectra were observed at 60 MHz using a JEOL JNM-FW 60 spectrometer in a temperature range between 300 and 110 K and at 77 K.

Results and Discussion

Figure 1 shows the temperature dependence of ^{69}Ga NQR frequencies in $[(CH_3)_4N]_2Ga_2Br_6$. Three weak ^{69}Ga NQR lines were observed at 77 K and intensities of these lines increased on raising the temperature to 83 K. Another resonance line appeared at 83 K. The discontinuous change of the temperature dependence took place at 98 K and four NQR lines reduced to three. On further increasing the temperature, three lines reduced to two at 137 K. Accordingly we infer that phase transitions take place at 98 and 137 K. Figure 2 shows the temperature dependence of ^{81}Br NQR frequencies. The ^{81}Br NQR lines observed between 77 and 137 K were too weak to measure accurately the frequency variation especially above 98 K. Five NQR lines were observed above 137 K. A differential thermal analysis (DTA) experiment was carried out above 100 K using a homemade apparatus. On heating, an endothermic peak with a small shoulder at

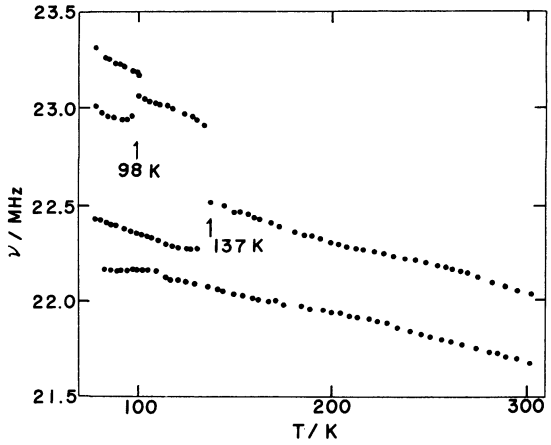

Fig. 1. Temperature dependence of ^{69}Ga NQR frequencies in $[(CH_3)_4N]_2Ga_2Br_6$.

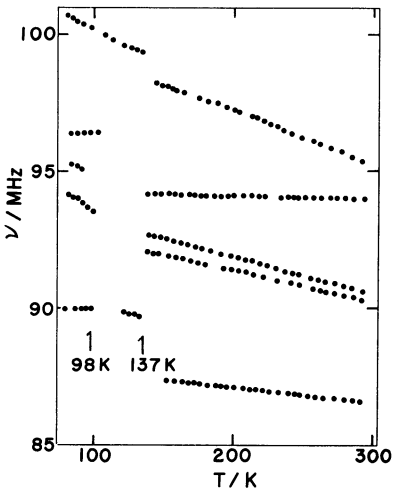

Fig. 2. Temperature dependence of ^{81}Br NQR frequencies in $[(CH_3)_4N]_2Ga_2Br_6$.

ca. 135 K appeared at 137 K. Unsymmetrical DTA peaks with a long tail on the low-temperature side were reported for $(CH_3NH_3)_2PtX_6$ (X=Cl, Br, and I) and attributed to the structural phase transitions related to the rearrangement of the octahedral anions PtX_6^{2-}.[5] In $[(CH_3)_4N]_2Ga_2Br_6$, it can be considered that the phase transitions at 98 and 137 K are related to motions of the $(CH_3)_4N^+$ ion.

The temperature dependence of the second moment M_2 of ^1H NMR spectra is shown in Fig. 3. On cooling, M_2 showed a constant value of ca. 0.5×10^{-8} T^2 down to ca. 140 K, while it increased rapidly below ca. 140 K and reached 20.1×10^{-8} T^2 at 77 K. According to the M_2

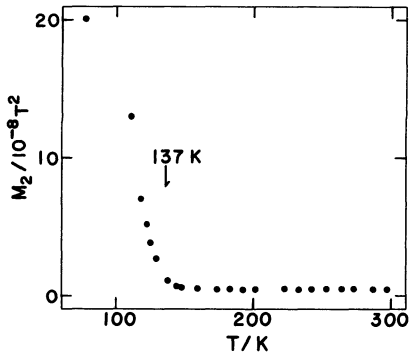

Fig. 3. Temperature dependence of the ^1H NMR second moment in $[(CH_3)_4N]_2Ga_2Br_6$.

calculation for $(CH_3)_4NX$(X=Cl, Br, and I),[4] the theoretical M_2 values in these halides are as follows: ca. 30×10^{-8} T^2 for the rigid lattice; ca. 11×10^{-8} T^2 for the rotaion of all methyl groups about C_3 axes; ca. 1×10^{-8} T^2 for the isotropic reorientation of $(CH_3)_4N^+$ ion. Accordingly, motions of the cation in $[(CH_3)_4N]_2Ga_2Br_6$ freeze for the most part at 77 K and the isotropic reorientation takes place above 140 K. On the other hand, a single ^{69}Ga NQR line was observed in $[(CH_3)_4N]_2Ga_2Cl_6$ and its frequency decreased monotonously from 23.37 MHz at 77 K to 22.68 MHz at 293 K with increasing temperature. The M_2 values of ^1H NMR spectra were 0.5×10^{-8} T^2 above 110 K and 11.3×10^{-8} T^2 at 77 K. Accordingly the rotation of the methyl group takes place even at 77 K for the chloro-complex. We predict that the phase transitions in $[(CH_3)_4N]_2Ga_2Br_6$ at 98 and 137 K can be ascribed to the onset of the isotropic reorientation of the $(CH_3)_4N^+$ ion and/or the rotation of the methyl groups. The occurence of these motions leads to the highly symmetric structure of the crystal being consistent with the fact that the number of the ^{69}Ga NQR lines decreased above these transition temperatures.

Figure 4 shows the temperature dependence of the ^{81}Br and ^{69}Ga NQR frequencies in $[(C_2H_5)_4N]_2Ga_2Br_6$. The single ^{69}Ga NQR line observed was so weak and broad between 77 and 118 K that we could not determine the resonance frequency accurately. A similar phenomenon was also observed for the above-mentioned $[(CH_3)_4N]_2Ga_2Br_6$, although the reason of the broadening is unknown. On heating, the resonance line became sharp and could be observed from 118 K up to 308 K, above which the resonance line disappeared. Three ^{81}Br lines which could be seen at low temperatures disappeared at ca. 275 K when the temperature was increased. The disappearance of the NQR lines can be attributed to the onset of the C_3 reorientation of the $GaBr_3$ group about the Ga-Ga bond for the following reasons. If the $Ga_2Br_6^{2-}$ ion has

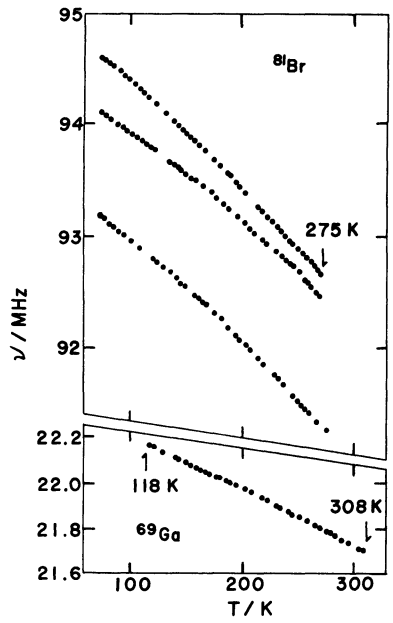

Fig. 4. Temperature dependences ^{81}Br and ^{69}Ga NQR frequencies in $[(C_2H_5)_4N]_2Ga_2Br_6$.

a structure of D_{3d} symmetry, the C_3 reorientation of the $GaBr_3$ group about the C_3 axis must not affect the ^{69}Ga NQR line.[6,7] The $Ga_2Br_6^{2-}$ ion in $[(C_2H_5)_4N]_2Ga_2Br_6$, however, has no D_{3d} symmetry because three ^{81}Br NQR lines were observed. Therefore, we can expect that the asymmetry parameter of the ^{69}Ga EFG is not zero and the principal z-axis of the EFG tensor is not parallel to the Ga-Ga bond. In addition, two bulky $GaBr_3$ groups should have a high barrier for rotation about the C_3 axis. Accordingly, the onset of the C_3 reorientation gives so drastic change of the EFG's at both ^{81}Br and ^{69}Ga nuclei that it is probable that this motion causes the disappearance of the NQR lines.

References

1) T. Okuda, N. Yoshida, M. Hiura, H. Ishihara, K. Yamada, and H. Negita, *J. Mol. Struct.*, **96**, 169 (1982).

2) K. L. Brown and D. Hall, *J. Chem. Soc., Dalton Trans.*, **1973**, 1843.

3) C. A. Evans and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, **1969**, 1201.

4) M. Mahajan and B. D. Nageswara Rao, *J. Phys. Chem. Solids*, **33**, 2191 (1972).

5) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

6) R. Sh. Lotfulin and G. K. Semin, *Phys. Status Solidi*, **35**, 133 (1969).

7) J. L. Ragle, *J. Phys. Chem.*, **63**, 1395 (1959).