

LOCAL ELECTRIC FIELD GRADIENTS AND BARRIERS TO HINDERED ROTATION IN COMPLEX GALLIUM DEUTERIDES

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Complex gallium hydrides MGaH_4 , where M is an alkali metal, are ionic compounds. They crystallize in the orthorhombic system with space group C_{mnm} for NaGaH_4 and P_{nma} for the potassium, rubidium, and cesium salts; $Z = 4$ [1]. Their crystal lattices are composed of compact GaH_4^- anions and alkali-metal cations M^+ . The GaH_4^- anion is a distorted tetrahedron with the Ga–H distances falling within 1.497–1.538 Å and a nearly tetrahedral H–Ga–H angle (109.7°) [2, 3]. The degree of distortion of the anion depends on the type of cation and manifests itself in the magnitude of the electric field gradient (EFG) in the gallium positions. The effect of the crystal lattice on the EFG distribution makes itself evident in the magnitude of the EFG in the cationic positions [4]. In this paper, we report on the results of measuring the spin-lattice relaxation time of deuterium (T_1) and the quadrupole coupling parameters (the quadrupole coupling constant (QCC) C_Q and the asymmetry parameter of the EFG tensor η) at the deuterium, gallium, and cation sites in the crystalline tetrahydridogallates NaGaD_4 , $\text{NaGa}(\text{H}_{2.6}\text{D}_{1.4})$, KGaD_4 , $\text{KGa}(\text{H}_{2.6}\text{D}_{1.4})$, RbGaD_4 , and CsGaD_4 . CW and pulsed ^2H , ^{23}Na , ^{39}K , ^{87}Rb , ^{133}Cs , and $^{69,71}\text{Ga}$ NMR measurements in the fields $B_0 = 1.4$, 1.88, and 7.04 T were taken in the temperature range 95–375 K. At all the B_0 values, the ^{39}K , ^{87}Rb , and $^{69,71}\text{Ga}$ NMR line shape is represented only by the central $\pm 1/2$ transition dominated by the second-order quadrupole effects, whereas the ^{23}Na and ^{133}Cs NMR line shape is represented by a satellite contour caused by the first-order quadrupole effects. For all the positions (cation, gallium, deuterium), temperature-induced changes in the NMR line shape indicate that the GaD_4^- or $\text{Ga}(\text{H}_{2.6}\text{D}_{1.4})^-$ anion is involved in hindered reorientation about its center of gravity over the allowed hydrogen/deuterium positions. In the temperature range under consideration, the reorientation of the anion completely averages the EFG at the deuterium and sodium sites. As temperature increases, the ^2H NMR line shape gradually changes from a doublet typical of a rigid lattice to a narrow singlet that corresponds to isotropic reorientation of the GaD_4^- anion. The activation energy E_a and the correlation time τ_0 of

reorientations were determined from the temperature dependence $T_1(^2\text{H})$, which has a typical V-shape form with a minimum. The QCCs for ^2H for the rigid lattice C_Q^* were calculated from the $T_{1\min}(T)$ values. These QCCs were compared to the corresponding C_Q values determined from the doublet contour of the ^2H NMR spectrum at $\eta \leq 0.1$. In the positions of the gallium isotopes and cation nuclei (K, Rb, Cs), the QCC values are not averaged since neither the rotation of the GaD_4^- anion as a whole about its axes nor the exchange of positions of deuterium atoms does not alter the charge distribution about heavy atoms. The temperature dependences of the QCCs C_Q in the positions of gallium and alkali-metal cations (except for sodium) are weak ($-1 \times 10^{-4} \text{ K}^{-1}$) and are described by the formula

$$C_Q(T) = C_Q(0) \{1 - kT/8\pi^2 I \nu_l^2\},$$

where $C_Q(0)$ is the QCC extrapolated to $T \rightarrow 0$; I is the moment of inertia of GaD_4^- , $I = 21.4 \times 10^{-40} \text{ g}\cdot\text{cm}^2$; and ν_l is the libration frequency, $\sim 35 \text{ cm}^{-1}$. For KGaD_4 and RbGaD_4 , the asymmetry parameters η in the gallium and cationic positions decrease with increasing temperature and have virtually the same temperature dependence as C_Q . This is evidence of a small variation in the difference between the q_{xx} and q_{yy} components of the EFG tensor with changing temperature since

$$q_{xx} + q_{yy} + q_{zz} = 0, \eta = |q_{yy} - q_{xx}| / q_{zz}, q_{zz} = hC_Q / e^2 Q.$$

For CsGaD_4 , the orientation of the tensor components in the anionic and cationic positions persists since $\eta(^{69,71}\text{Ga})$ increases with increasing temperature due to a decrease in C_Q , whereas $\eta(^{133}\text{Cs})$ remains constant. For NaGaD_4 , the orientations and magnitudes of the EFG tensor components in the gallium positions change with temperature, which is associated with the structural phase transition at 290 K. The table presents the QCCs C_Q and asymmetry parameters η obtained at the lowest temperatures (100–115 K) and the activation parameters E_a and τ_0 for reorientational motion of the anion.

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Alkali-metal	Cationic position	GaD_4^- position	QCC ^2H , kHz	E_a	τ_0
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tetrahydridogallate	M ⁺	QCC MHz	η	QCC, MHz (± 0.3)		η ± 0.20	C _Q [*] (± 7)	C (± 2)	kJ/mol $\pm 10\%$	$\times 10^{-16}$ s $\pm 40\%$
				⁶⁹ Ga	⁷¹ Ga					
NaGaD ₄	²³ Na	0.5	0.44	-	-	-	89.6	70	34.7	3.1
NaGaH _{2.6} D _{1.4}				5.9	3.8	0.50	90.6	67	35.2	2.1
KGaD ₄	³⁹ K	0.61	0.5	7.2	4.8	0.46	78.0	60	38.3	24
KGaH _{2.6} D _{1.4}				6.9	4.5	0.51	78.0	72	40.6	7.7
RbGaD ₄	⁸⁷ Rb	3.42	0.25	7.4	4.9	0.48	83.8	65	33.5	65
CsGaD ₄	¹³³ Cs	0.14	0.1	6.8	4.2	0.38	86.3	76	25.8	140

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