Temperature Dependence of NQR Spectra and Phase Transitions in Alkali Metal Hexaiodozirconates and Hafnates (IV) *

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Hexaiodometallates of the type R_2MI_6 (R = Li, Na, K, Rb, Cs; M = Zr, Hf) have been studied over a wide temperature region using ^{127}I NQR. They show a notable diversity of structures. The values of the ^{127}I $e^2 Q q/h$ in hafnates appeared to exceed those in related zirconates by about 10%. This, together with the more positive temperature coefficients of the NQR spectra in zirconates is accounted for by a slightly greater π-character in the Zr–I than the Hf–I bonds in related compounds. Several 1st and 2nd order phase transitions have been detected in Na_2MI_6 (I) and Rb_2MI_6 (II). In (I) the high-temperature phase has a structure of lower symmetry than the low-temperature phase, and the 1st order phase transition point reveals an extremely large range of hysteresis.

Introduction

Much information obtained using NQR on hexahalometallates of Groups VI–VIII transition metals is now available and has been reviewed [1–3]. Crystal and electronic structures, lattice dynamics and phase transitions (PT) have been extensively studied in a number of compounds. This paper gives the results of a ^{127}I NQR study on previously unknown hexahalometallates (IV), namely alkali metal hexaiodozirconates and hafnates (IV)′ carried out over a wide range of temperatures.

Experimental

The preparation of several title compounds has been described earlier [4, 5]. The remaining salts were prepared similarly. The temperature of the reaction zone varied from compound to compound; it was firstly raised to the melting point of the salt (or to the point of peritectic conversion of the Na salts, melting incongruently) and then allowed to fall to 20–50° below this point, at which level it was maintained for approximately 30 min. All manipulations excluded contact of the reactants with air moisture. Some of the compounds were analyzed using DTA and XPA. NQR measurements have been carried out using a pulse spectrometer operating within the range 10–300 MHz (SKB IRE AN SSSR).

Results and Discussion

The ^{127}I NQR data of the compounds studied are listed in Table 1 for several temperatures. Some of them are seen to change multiplicity with temperature. Hence we have studied the temperature dependence of the ^{127}I transition frequencies and derived the values of $e^2 Qq/h$ (QCC) (Figures 1–4). The results indicate that both pairs, $\mathbf{Li_2MI_6}$ and $\mathbf{Cs_2MI_6}$ (M = Zr, Hf), form regular $[MI_6]^{2-}$ octahedra at all temperatures studied, the spectral singlets showing a linear dependence on temperature with positive coefficients (Figure 1). The latter are evidently greater in the Zr than in the Hf salts. According to XPA the salts Li_2MI_6 crystallize in a body-centered cubic Im 3m lattice with unit cell dimensions $a = 13.61$ and 13.57 Å for the Zr and Hf respectively. Both Cs_2MI_6 salts have a body-centered cubic Fm 3m lattice, $a = 11.613$ Å in Cs_2ZrI_6 and $a = 11.609$ Å in Cs_2HfI_6 [4, 6], with a bonding distance Hf–I = 2.829(2) Å and an interatomic distance Cs–I = 4.105(1) Å [6].

$\mathbf{Na_2ZrI_6}$ and $\mathbf{Na_2HfI_6}$ give singlet NQR spectra at low temperatures only (Figure 2). On heating the Zr salt to +65 °C and the Hf salt to +90 °C, a 1st order phase transition (PT) occurs with discontinuities in the temperature curves. The spectra of the high-temperature (HT) phases appear with a large split-

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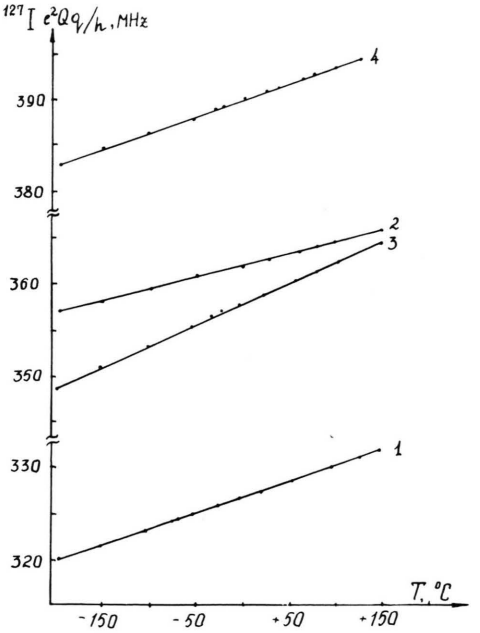

Fig. 1. Temperature dependence of the ^{127}I quadrupole coupling constants (e^2Qq/h) in the compounds: Li_2ZrI_6-1; Li_2HfI_6-2; Cs_2ZrI_6-3; Cs_2HfI_6-4.

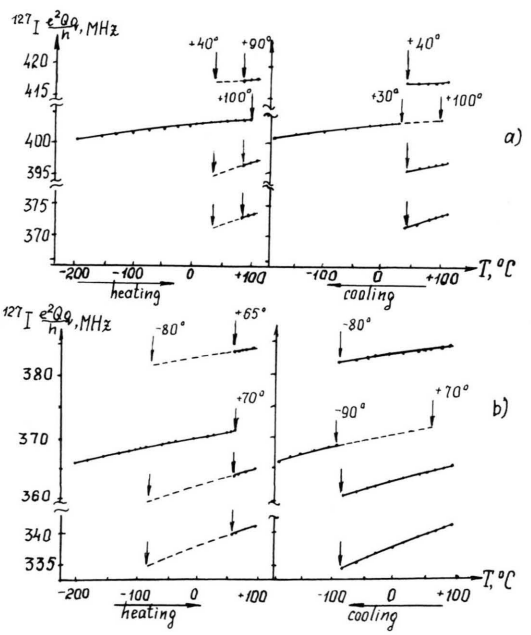

Fig. 2. Temperature dependence of the ^{127}I quadrupole coupling constants (e^2Qq/h) in Na_2HfI_6 (a) and Na_2ZrI_6 (b) on heating (left) and on cooling (right). The dotted lines show the range of hysteresis.

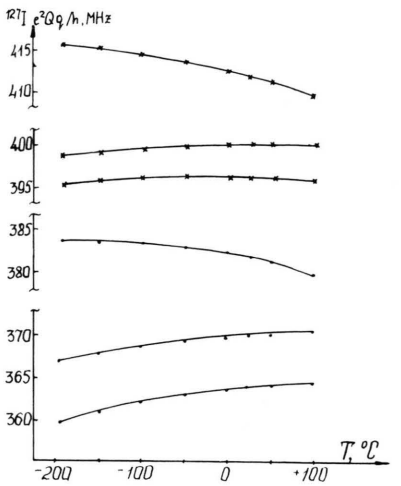

Fig. 3. Temperature dependence of the quadrupole coupling constants ($^{127}I\,e^2Qq/h$) in K_2ZrI_6 (circles) and K_2HfI_6 (crosses).

ting and increased asymmetry parameters η [7]. NQR displays in this case a rare situation when the HT phase has a structure of lower symmetry (presumably monoclinic) than the low-temperature (LT) phase. If a temperature run is reversed, starting from +100 °C, the HT resonances exist in Na_2ZrI_6 down to −80 °C while those of the LT phase reappear at −90 °C only, revealing an extremely large hysteresis of the PT point. The temperature changes of Na_2HfI_6 are of similar type but show a smaller range of hysteresis. **K_2ZrI_6** and **K_2HfI_6** give split ^{127}I NQR spectra (Table 1) showing inequivalence of the M−I bonds in the $[MI_6]^{2-}$ anions due to their distortion. The preliminary XPA data show a symmetry not higher than monoclinic in both salts. The distortion of the octahedra might be caused by interionic interactions associated with elongation of the corresponding M−I bonding distances. Since the d^0 configuration of the complexes assumes vacancies in their d_ε^* orbitals suitable for accepting p_π electron density from halogens, the elongation of the M−I bond is expected to reduce its $p_\pi-d_\pi$ character. This, according to the Townes and Dailey theory [8], will shift the corresponding ^{127}I resonance to higher frequencies with respect to those displayed by the atoms not disturbed by interionic interactions. The other spectral evidence for interionic contacts is provided by the temperature dependence. The relatively increased σ-character of

Table 1. ^{127}I NQR spectra of alkali metal hexaiodozirconates and hafnates (IV).

R	T, K	Compounds of the type R_2ZrI_6				Compounds of the type R_2HfI_6			
		Transition freqs. (MHz) 1/2–3/2	3/2–5/2	e^2Qq/h (MHz)	η (%)	Transition freqs. (MHz) 1/2–3/2	3/2–5/2	e^2Qq/h (MHz)	η (%)
Li	77	48.15	96.03	320.2	4.7	53.65	107.08	357.0	4.0
	300	49.29	98.17	327.4	5.8	54.52	108.68	362.2	5.5
Na	77	55.00	109.79	366.1	3.9	60.27	120.23	400.9	4.5
	300[a]	55.67	111.10	370.4	4.0	60.66	120.96	403.4	4.7
	300[b]	51.69	101.08	338.35	13.1				
		62.51	106.05	363.15	38.1				
		65.50	111.95	383.0	37.5				
K	77	55.32	107.51	359.8	14.0	60.40	118.22	395.2	13.1
		56.71	109.52	366.8	16.4	61.25	119.10	398.7	14.9
		61.96	113.33	383.3	27.2	66.32	123.28	415.6	24.5
	300	55.25	108.85	363.1	10.8	60.17	118.61	396.1	10.1
		56.70	110.52	369.8	14.1	61.01	119.62	400.0	12.8
		60.11	113.42	381.6	21.7	64.32	122.61	411.8	19.5
Rb	77	53.38	106.57	355.1	4.3	58.30	116.315	387.9	4.3
		55.16	106.82	357.5	16.3	59.96	116.73	390.75	14.6
		56.02	108.04	362.1	17.1	60.75	118.95	395.0	15.3
	300	52.84	105.61	352.0	2.4	58.22	115.68	386.0	7.2
		53.75	106.25	354.9	9.5	57.25	114.52	381.7	0.0
	373	52.40	104.73	349.1	0.0	57.12[c]	114.14[c]	380.5[c]	2.6[c]
Cs	77	52.29	104.53	348.5	1.9	57.71	114.99	383.0	4.3
	300	53.85	107.69	359.0	0.8	58.74	117.40	391.4	0.0

[a] After cooling to 77 K; [b] After heating above +65 °C; [c] At 403 K.

the elongated bond will evidently produce a negative contribution to the temperature coefficient of this line.

As one can see from Fig. 3, one of the ^{127}I signals is shifted to higher frequencies with respect to the doublet, and its temperature dependence is negative, in contrast to the positive temperature coefficients of the doublet lines. This, as well as the larger values of η for the high-frequency singlets supports the suggestion of interionic interactions in the potassium salts. **Rb_2ZrI_6** and **Rb_2HfI_6** undergo several phase transitions (Figure 4). Two weak endothermal peaks have been observed (−18 °C, +81 °C in the Zr salt; −23 °C, +81 °C in the Hf salt) on their DTA curves [9]. NQR confirms these results and reveals one more PT near room temperature (PT-3 in Figure 4). It is characterized by a change in the d(QCC)/dT value. The PT's of similar appearance observed at −16 °C in K_2ReBr_6 (Fig. 5a) and at −52 °C in K_2SeBr_6 have been accounted [1] for by torsional oscillations of the $[MBr_6]^{2-}$ ions about one of the M–Br axes, so that the corresponding resonances are insensitive to the PT. In the $RbMI_6$ compounds the nature of PT-3 might be similar but the axes of torsional oscillations can hardly coincide with any of the M–I bonding directions since all the spectral lines are sensitive to this PT.

A great number of R_2MX_6 antifluorite compounds are at present known [2] which show NQR temperature dependences resembling those in Figure 4. Thus, compounds like Rb_2MI_6, K_2SnBr_6 and K_2TeBr_6 have three component NQR spectra in their LT phases [2], indicating a symmetry of the crystals lower than tetragonal. Indeed it is monoclinic in K_2TeBr_6 with a space group $P2_1/n$ [10]. Above the low-temperature PT point, Rb_2MI_6 gives two-component spectra, the symmetry of the salts becoming tetragonal with probable space group P4/nc or P4/mnc and unit cell dimensions $a = 8.090$, $c = 11.771$ Å and $a = 8.076$, $c = 11.673$ Å for the Zr and Hf salts, respectively.

In the known antifluorite compounds, a tetragonal phase appears on cooling the cubic K_2PtCl_6-type crystals below the PT point. The PT involves, as in K_2ReCl_6, a gradual rotation of the $[MX_6]^{2-}$ anions through a small angle θ around the z axis [11]

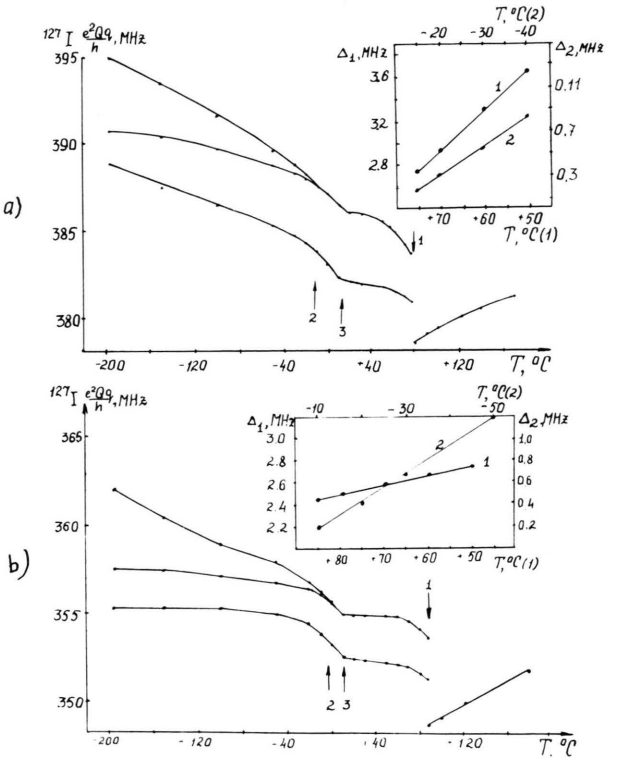

Fig. 4. Temperature dependence of the ^{127}I quadrupole coupling constants (e^2Qq/h) in Rb_2ZrI_6 (a) and Rb_2HfI_6 (b). Arrows show the phase transition (PT) points. In the inserts, the temperature dependence of the spectral splitting ($\Delta = e^2Qq_i/h - e^2Qq_j/h$) below the PT-1 ($\Delta_1$) and PT-2 ($\Delta_2$) is shown. Above PT-2 $\Delta_2 = 0$.

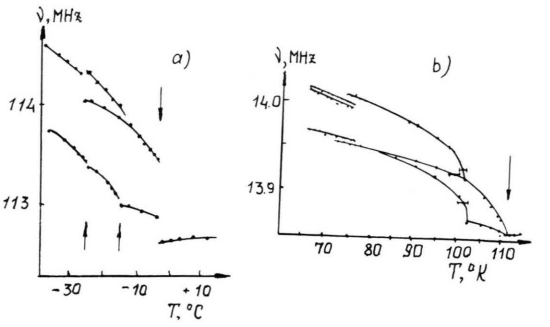

Fig. 5. a) Temperature dependence of ^{79}Br NQR frequencies in K_2ReBr_6 [1]. Arrows show the phase transition (PT) points. b) Temperature dependence of ^{35}Cl NQR frequencies in K_2ReCl_6 [11]. Arrow shows the PT point from the cubic to tetragonal phase.

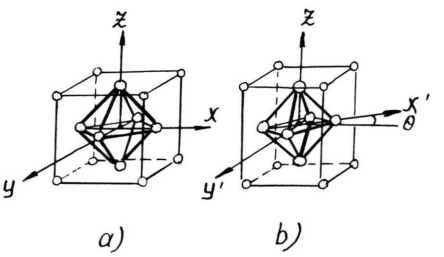

Fig. 6. Orientation of the $[ReCl_6]^{2-}$ anions in the cubic (a) and tetragonal (b) modifications of K_2ReCl_6 [2].

(Figure 6). The NQR signal observed in the cubic phase undergoes only a slight frequency shift below the PT point (Fig. 5b). The octahedra remain undistorted in the LT phase that is characterized by small tetragonal distortion of the R cation cage. The mechanism of the PT in K_2ReCl_6 was attributed [11] to a soft rotary mode of the $[ReCl_6]^{2-}$ anion, the force constant of which is markedly temperature dependent and vanishes at the PT point. It was also shown in NQR temperature dependence studies of antifluorites [3, 12] that $\Delta\nu \sim A\theta^2$, where $\Delta\nu$ is the spectral splitting several degrees below the PT point and A is constant. From the other side, the linear temperature dependence of $\Delta\nu$ within several degrees below the PT (Fig. 5b) indicates that $\theta \sim (T - T_0)^{1/2}$, in agreement with the Landau theory, θ being the order parameter. Using this approach, θ is estimated to be about 4° in K_2ReCl_6, 7° in K_2PtBr_6 and 11° in $(NH_4)_2PtBr_6$ [3].

It is to be noted that the octahedra remain undistorted not only in the tetragonal phase but also in the phases with symmetries lower than tetragonal [10, 12]. In the monoclinic phase of K_2TeBr_6, the $[TeBr_6]^{2-}$ octahedra are reported [10] to be regular (O_h), each being rotated through small angles successively around two axes of the unit cell.

One can therefore conclude that a displacive PT of 2nd order, when identified by NQR, is characterized by a temperature dependence of the spectra showing no appreciable discontinuity at the PT point with a spectral splitting varying linearly with temperature within a few degrees below the PT point.

As Fig. 4 shows, these very features characterize the low-temperature PT (PT-2) in both Rb salts. The high-temperature PT (PT-1) shows however a slight discontinuity indicating that volume effects, π-bonding effects, etc. might contribute to the

Table 2. The M–I chemical bond characters i, σ, π and temperature coefficients of the quadrupole coupling constants (e^2Qq/h) in the high-symmetry phases of alkali metal hexaiodozirconates and haftnates (IV) according to ^{127}I NQR.

Compounds of the type R_2ZrI_6					Compounds of the type R_2HfI_6			
R	i	σ	π	$\frac{d(e^2Qq/h)}{dT}$ (kHz/deg.)	i	σ	π	$\frac{d(e^2Qq/h)}{dT}$ (kHz/deg.)
Li	0.21	0.356	0.434	+33.7	0.20	0.371	0.429	+24.9
Na	0.21	0.370	0.420	+18.8	0.20	0.383	0.417	+ 9.8
Rb	0.21	0.365	0.425	+49.2	0.20	0.377	0.423	+41.0
Cs	0.21	0.365	0.425	+45.7	0.20	0.378	0.422	+35.0

change in EFG at the PT point [3]. But the temperature behaviour of the spectral splitting below the PT point resembles that in antifluorites (see inserts in Fig. 4), allowing one to think that this PT also occurs from a cubic phase and involves rotation of the $[MI_6]^{2-}$ octahedra.

Summarizing the results obtained, we must note that the ^{127}I QCC values in all the hafnates appear to exceed those in related zirconates by about 10% (Table 1), although the Zr and Hf atoms have very similar atomic ($R_{Zr} = R_{Hf} = 1.55$) and ionic ($Zr^{+4} = 0.79$; $Hf^{+4} = 0.78$) radii and electronegativities ($\chi_{Zr} = 1.22$; $\chi_{Hf} = 1.23$) [13]. Since Figs. 1–4 show the positive temperature coefficients of the ^{127}I QCC values to be greater in the Zr than in the Hf salts, we assume that these differences originate partly from the relatively higher π-character of the Zr–I than the Hf–I bonds in related pairs. In order to get a quantitative view of the extent of the variation in bonding parameters sufficient to produce the observed differences in the QCC values, we have calculated within the approximations of the Townes and Dailey theory [8] the M–I bonding character in the high-symmetry modifications of the compounds studied (Table 2). The extents of ionic, σ-covalent and π-covalent character are denoted by i, σ and π, respectively. Assuming that $i + \sigma + \pi = 1$, $\pi_x + \pi_y = \pi$, and neglecting s-hybridization of the σ-bonding orbitals, we have

$$\frac{e^2Qq}{e^2Qq_{at}} = \frac{N_x + N_y}{2} - N_z = \sigma - \frac{\pi_x + \pi_y}{2} = \sigma - \frac{\pi}{2}$$
$$= 1 - i - \tfrac{3}{2}\pi .$$

Here N_j ($j = x, y, z$) are the occupancies of the valence p_j orbitals on the iodine atom. They are evidently equal to: $N_z = 2 - \sigma$, $N_x = 2 - \pi_x$, $N_y = 2 - \pi_y$; we take $e^2Qq_{at}/h = 2292.7$ MHz [14]. The value of i was determined from electronegativity differences [13]. The reliability of the numerical values of i, σ, π so obtained is of course not high. They are however useful to show that the measured difference between the ^{127}I QCC values in the related pairs of compounds can be produced by tiny variations in the M–I bonding parameters, the greater π-values of the Zr–I bonds relative to the Hf–I bonds contributing to the observed difference.

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