Cesium Iodometallates(III), $Cs_3M_2I_9$, with M = Rare Earth. A Structural Investigation by ^{127}I NQR *

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The ^{127}NQR spectra of cesium enneaiododimetallates $Cs_3M_2I_9$, M = Dy, Ho, Er, Yb, Y and Tb, Sm, Nd, Pr have been studied as a function of temperature. The compounds are characterized by X-ray powder diffraction, too. The first group of compounds, M = Dy ··· Y, belongs to the family of $Cs_3Cr_2Cl_9$-type enneahalogenodimetallates (III). The crystal structure of the second group, M = Tb ··· Pr, is less symmetric, as in the ^{127}I NQR the presence of two crystallographically independent iodines shows up. Nuclear quadrupole coupling constants for the terminal and bridging halogens have been calculated from the NQR frequencies. The dependence of the NQR frequencies and of the crystal structure from the radius of the $RE^{3\oplus}$-ion is discussed. The NQR spectra reveal phase transitions of the investigated enneaiododimetallates(III), for which T_{tr} also depends on $r(RE^{3\oplus})$. Positive temperature coefficients of the ^{127}I have been found and the influence of π-bond character is considered.

Introduction

Alkali metal chlorometallates(III) with rare earth RE(III) elements are well known. In contrast, little is available in literature on iodometallates(III). Kutscher and Schneider [1], by differential thermal analysis (DTA) investigations, observed, that two congruently melting compounds exist in nearly each systems $AI-REI_3$ (A = alkali metal, RE = rare earth): The enneaiododimetallates(III) $A_3RE_2I_9$ and the hexaiodometallates(III) A_3REI_6. Especially large size cations $A^{\oplus}$, such as $Cs^{\oplus}$, stabilize the complex $A_3RE_2I_9$; congruent melting ennenaiododimetallates(III) exist only for $A = Cs^{\oplus}$.

The crystal structure of $Cs_3Y_2I_9$ was determined by Guthrie et al. [2], and Wang et al. determined the structure of $Cs_3Tm_2I_9$ [3]. They found these enneaiodides to be isostructural, belonging to the $Cs_3Cr_2Cl_9$-type [4] compounds. From structure field maps of enneachloro- and enneabromo-dimetallates(III) Meyer and Schönemund [5] predicted that all enneaiododimetallates(III) should be isostructural.

We were interested in applying ^{127}I nuclear quadrupole resonance, NQR, to a comparative structural study of complex iodometallates(III) with $RE^{3\oplus}$. In literature, Babushkina et al. [6] have reported ^{127}I NQR experiments on $Rb_3Sm_2I_9$ (and $KSmI_4$, $RbHoI_4$). Iodoholmates(III) have been studied with ^{127}I NQR by Dudareva et al. [7].

Experimental

Preparation

Not much is reported in literature on the synthesis of complex alkali metal iodometallates(III), $A_3M_2I_9$, with M = RE. Several authors have shown the existence of the compounds by DTA [1, 8, 9].

The cesium rare earth enneaiodides were prepared acording to

$$3\,CsI + 3\,I_2 + 2\,RE \rightarrow Cs_3RE_2I_9$$

as follows.

Stoichiometric amounts of CsI (Aldrich, 99.9%), RE-metal (Aldrich, 99%), and iodine (sublimated twice and dried over P_2O_5) were melted together in a sealed quartz tube. The temperature was raised slowly during two days to $T = 30$ K above the expected melting point (as reported in [1]) of the wanted compound. Then the sample was cooled down, slowly during 5 days, to room temperature to produce a crystallized

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Table 1. Synthesis of cesium enneaiododimetallates(III) with M^{3+} = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, and Y. T_{max} is the maximum heating temperature of the melt; T_m is the melting point of the compound.

Compound	CsI/g	I_2/g	M/g	T_{max}/°C	T_m/°C
$Cs_3Y_2I_9$	11.691	11.421	2.667	700	618
$Cs_3Yb_2I_9$	10.912	10.660	4.845	700	660
$Cs_3Er_2I_9$	12.249	11.966	5.258	690	662
$Cs_3Ho_2I_9$	8.492	8.296	3.594	680	627
$Cs_3Dy_2I_9$	10.353	10.112	4.316	670	646
$Cs_3Tb_2I_9$	11.691	11.421	5.018	670	608
$Cs_3Gd_2I_9$	11.691	11.421	4.718	620	588
$Cs_3Sm_2I_9$	11.691	11.421	4.511	570	557
$Cs_3Nd_2I_9$	11.691	11.421	4.327	550	514
$Cs_3Pr_2I_9$	11.691	11.421	4.227	530	470

Table 2. The lattice constants of the cesium enneaiododimetallates(III) of $Cs_3Cr_2Cl_9$-type crystal structure (space group $P6_3/mmc$). * This work.

Comp.	a/pm	c/pm	c/a	V_{elem}/pm^3	Lit.
$Cs_3Y_2I_9$	839.8(7)	2128.9(18)	2.535	1300.2(13)	*
$Cs_3Yb_2I_9$	836.4(9)	2115.9(34)	2.530	1282.0(20)	*
$Cs_3Er_2I_9$	838.8(13)	2120.4(21)	2.529	1292.4(21)	*
$Cs_3Ho_2I_9$	838.3(10)	2125.8(22)	2.536	1293.8(17)	*
$Cs_3Dy_2I_9$	838.5(12)	2125.8(29)	2.535	1294.5(20)	*
$Cs_3Y_2I_9$	840.6(1)	2128.0(1)	2.532	1302.2	[2]
$Cs_3Tm_2I_9$	838.5(1)	2118.0(4)	2.526	1289.6	[3]

sample as perfect as possible for the NQR experiments. In Table 1 the compounds synthesized, the in-weights, the maximum temperature of the heating, and the measured melting points are given.

Due to the reaction

$$2\,ReI_3 + SiO_2 \rightarrow SiI_4 + 2\,REOI\,,$$

taking place at high temperatures, it is of advantage to keep the reaction temperature as low as possible [10]. Because of the high sensitivity of the compounds $Cs_3RE_2I_9$ to moisture, all treatments of these compounds were carried out within a nitrogen filled glove box.

^{127}*I NQR*

To study the ^{127}I-NQR spectra of the cesium enneaiododimetallates(III), a superregenerative spectrometer with a frequency range $9 \le v/\mathrm{MHz} \le 80$ was used. The temperature dependence of the NQR spectra was measured over the range $100 \le T/\mathrm{K} \le 430$ using a temperature controlled nitrogen gas stream. The accuracy in measuring the temperature at the sample site is $\approx \pm 0.2$ K. At 77 K the sample holder was placed in a liquid nitrogen bath. The frequencies listed here are accurate to ± 5 kHz, being determined by the width of the ^{127}I NQR lines.

X-ray Powder Diffractometry

To characterize the synthesized compounds, X-ray powder diffraction photographs (Debye-Scherrer camera, radius = 57.30 mm, CuKα radiation, nickel filtered) were taken. Due to the strong absorption fairly long exposure times (≈ 20 h) were necessary. The theoretical X-ray powder diffraction pattern of $Cs_3Y_2I_9$ ($Cs_3Cr_2Cl_9$-type structure) has been calculated with the program LAZY PULVERIX [11] and compared with the observed diagrams. In case of isomorphism ($Cs_3Cr_2Cl_9$-type) the powder diffraction patterns were indexed and the lattice constants extracted were refined by least squares procedure.

Results

Cesium enneaiododimetallates(III), $Cs_3M_2I_9$, M = Dy, Ho, Er, Yb, Y

A comparison of the X-ray powder diffraction data with the results of the single crystal structure determination of $Cs_3Y_2I_9$ [2] showed that the five enneaiodides $Cs_3M_2I_9$, M = Dy, Ho, Er, Yb, and Y are isostructural, crystallizing with the space group D^4_{6h}-$P6_3/mmc$; there are $Z = 2$ formula units in the elementary cell. In Fig. 1a calculated X-ray powder pattern for $Cs_3Y_2I_9$ is compared with the one we found for $Cs_3Ho_2I_9$. All the powder diffraction diagrams were indexed and the lattice constants calculated by least squares methods [12]. In Table 2 the data are given. We note, that the radius of $M^{3\oplus}$ (Goldschmidt scale) in this group, crystallizing with the $Cs_3Cr_2Cl_9$-type structure, is ≤ 107 pm, the upper limit given by $r(Dy^{3\oplus}) = 107$ pm.

The compounds $Cs_3M_2I_9$ of the $Cs_3Cr_2Cl_9$-type structure should be described as cesium tri-μ-iodohexaiododimetallates(III). The iodines are octahedrally coordinated around the atom M^{3+} (RE^{3+}); the situation is sketched in Figure 2. Within the unit cell, two octahedra are connected by a common face, and thereby the anion $[RE_2I_9]^{3\ominus}$ contains three bridging iodine atoms (B) and 6 terminal iodines (A).

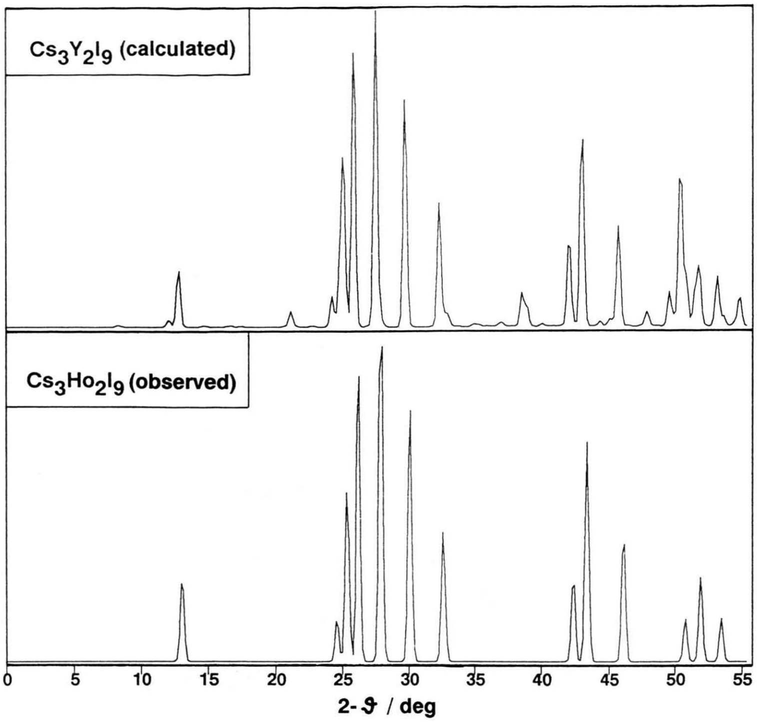

Fig. 1. Comparison of the X-ray powder diffraction diagrams of $Cs_3Cr_2Cl_9$-type (D_{6h}^4-$P6_3/mmc$, $Z=2$) cesium enneaiododimetallates(III). The upper spectrum shows the calculated line pattern of $Cs_3Y_2I_9$, the lower one the measured diffractogram of $Cs_3Ho_2I_9$.

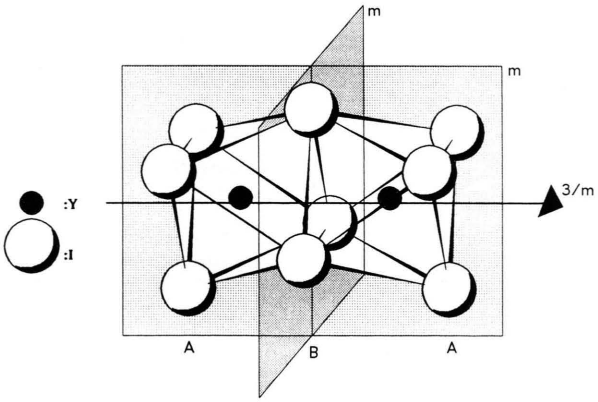

Fig. 2. Sketch of the bi-octahedral unit $[RE_2I_9]^{3\ominus}$ in the unit cell of the $Cs_3Cr_2Cl_9$-type ($P6_3/mmc$, $Z=2$).

Table 3. ^{127}I NQR frequencies at room temperature $T \approx 293$ K of the cesium enneaiododimetallates(III) with M^{3+} = Pr, Nd, Sm, Tb, Dy, Ho, Er, Yb, and Y (* different temperature).

Comp.	ν_1/MHz $1/2 \leftrightarrow 3/2$	ν_2/MHz $3/2 \leftrightarrow 5/2$	ν_3/MHz $1/2 \leftrightarrow 3/2$	ν_4/MHz $3/2 \leftrightarrow 5/2$
$Cs_3Dy_2I_9$	20.318	40.589	67.194	–
$Cs_3Y_2I_9$	21.299	42.567	69.710	–
$Cs_3Ho_2I_9$	21.686	43.389	69.349	–
$Cs_3Er_2I_9$	23.892	47.794	71.595	–
$Cs_3Yb_2I_9$	26.253	52.462	76.654	–
$Cs_3Tb_2I_9$	35.301	41.623	55.034	75.964
$Cs_3Sm_2I_9$	31.793	37.979	46.404	69.846
$Cs_3Nd_2I_9$	31.893	34.057	49.197	56.740 *
$Cs_3Pr_2I_9$	32.572 *	–	47.277 *	–

The ^{127}I NQR frequencies of the title compounds, at room temperature, are listed in Table 3. The two lower frequencies ν_1 ($m = \pm 1/2 \leftrightarrow m = \pm 3/2$) and ν_2 ($m = \pm 3/2 \leftrightarrow m = \pm 5/2$), the later one being about double of ν_1, rise from dysprosium ($\nu_1 = 20.32$ MHz) to ytterbium ($\nu_1 = 26.25$ MHz). These two transitions can be assigned to the bridging atoms (B). The temperature dependence of ν_1 and ν_2 were measured and the results are shown in Figure 3. The curves were fitted with the polynomial

$$\nu = \sum_{i=-1}^{2} a_i T^i . \tag{1}$$

The a_i are listed in Table 4. From the ^{127}I NQR spectra one recognizes easily that the five title compounds are isomorphous. They all show the same temperature dependence of the ^{127}I NQR, see Figure 3, with a positive temperature coefficient $d\nu(^{127}I)/dT$. This is

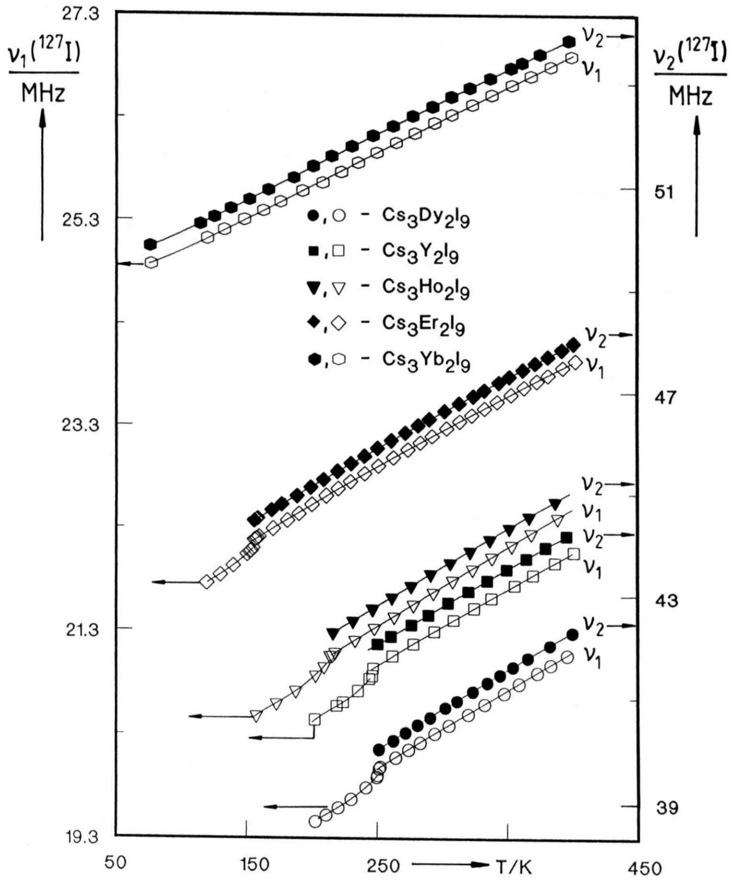

Fig. 3. $\nu_i(^{127}I)$ of the bridging iodine atoms (B-atoms) as functions of temperature ($Cs_3Cr_2Cl_9$-type cesium enneaiododimetallates(III)).

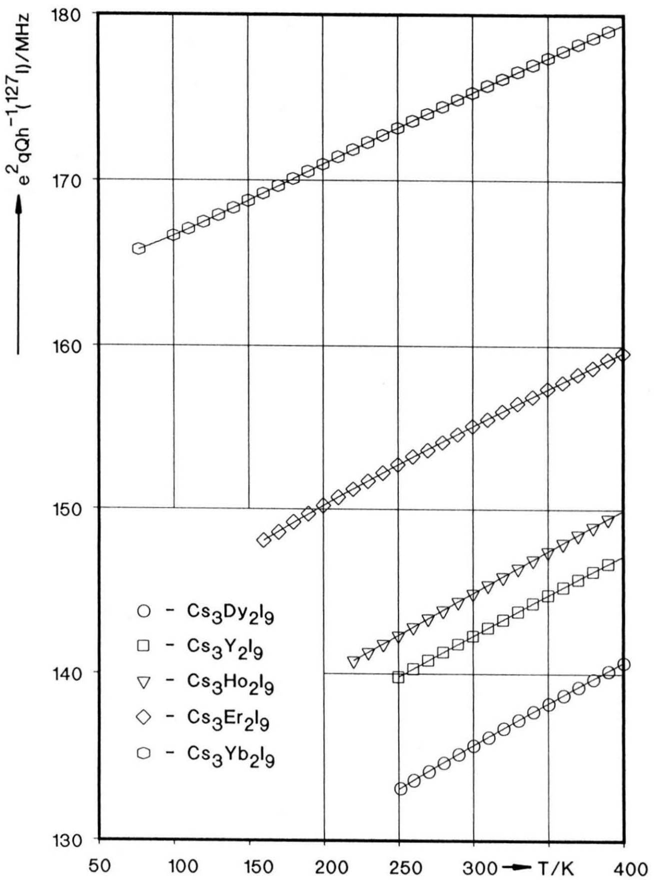

Fig. 4. The nuclear quadrupole coupling constants $e^2qQh^{-1}(^{127}I)$ of the $Cs_3Cr_2Cl_9$-type cesium enneaiododimetallates(III) as functions of temperature.

Table 4. ^{127}I NQR frequencies and parameters, $\nu(T) = a_0 + a_1 T + a_{-1} T^{-1} + a_2 T^2$ (comp. (2)). σ is the mean deviation of the calculated frequencies. The signal to noise ratio, S/N, was measured with lock-in technique, time constant = 10 s. N is the number of data points. $\Delta T = T_1 \dots T_2$ is the temperature range for which the parameterisation is valid.

Substance	ν/MHz		N	S/N	σ/kHz	a_0/MHz	$a_1 \cdot 10^3$/ MHz · K^{-1}	a_{-1}/ MHz · K	$a_2 \cdot 10^6$/ MHz · K^{-2}	ΔT/K
$Cs_3Y_2I_9$	ν_1	phase I	11	65	1	19.020	8.4405	−13.569	−1.7854	247−401
		phase II	6	4	1	124.01	−479.14	−7563.4	751.33	202−246
	ν_2	phase I	11	7	3	33.949	29.635	406.17	−16.597	252−397
$Cs_3Yb_2I_9$	ν_1	phase I	21	200	7	24.102	7.6075	15.564	−1.6799	77−398
	ν_2	phase I	21	50	8	48.161	15.904	30.540	−4.9395	77−398
$Cs_3Er_2I_9$	ν_1	Phase I	28	100	4	20.943	8.4711	−3.9139	−2.3450	156−402
		phase II	7	7	3	32.011	−83.571	−456.79	249.45	120−155
	ν_2	phase I	26	20	4	41.979	16.556	−12.074	−4.2783	156−402
$Cs_3Ho_2I_9$	ν_1	phase I	14	80	3	19.378	8.3468	−10.477	−1.1788	214−388
		phase II	5	7	4	46.917	−156.76	−1585.2	310.15	157−209
	ν_2	phase I	12	10	3	38.054	18.946	58.626	−5.0003	218−388
$Cs_3Dy_2I_9$	ν_1	phase I	14	90	1	19.433	3.7866	−155.26	3.4523	251−396
		phase II	7	10	5	85.583	−306.25	−4862.5	485.46	202−249
	ν_2	phase I	14	19	1	37.419	12.646	−184.17	1.1993	253−402
	ν_3	phase I	11	10	3	66.085	5.1137	−80.027	−1.6950	252−400
		phase II	4	3	1	−3537.3	14828	291784	−20318	235−248
$Cs_3Tb_2I_9$	ν_1	phase I	21	10	3	34.675	1.7655	60.673	−1.1304	119−398
		phase II	4	8	1	70.684	−375.76	−1124.3	1322.2	77−117
	ν_2	phase I	21	10	2	42.047	0.1580	−33.204	−4.2029	119−398
		phase II	4	8	1	48.913	−57.375	−220.92	107.23	77−117
	ν_3	phase I	21	10	3	52.471	9.3196	22.540	−2.7956	119−398
		phase II	4	10	1	122.05	−730.40	−2150.8	2579.8	77−117
$Cs_3Sm_2I_9$	ν_1	phase I	13	11	1	31.510	0.3659	44.000	0.2930	231−397
		phase II	10	10	22	34.679	−31.706	−125.17	89.100	77−229
	ν_2	phase I	13	13	1	36.346	6.2705	175.28	−9.3516	231−397
		phase II	11	17	15	38.464	12.764	88.172	−68.709	77−230
	ν_3	phase I	13	16	2	41.589	16.354	236.15	−9.0605	231−397
		phase II	10	8	3	47.852	−23.817	−110.54	68.969	77−229
$Cs_3Nd_2I_9$	ν_1	phase I	9	8	6	21.405	30.290	1119.6	−26.657	306−398
	ν_2	phase I	18	8	6	36.420	−6.1410	−206.28	2.0491	284−399
	ν_3	phase I	19	4	4	42.250	21.901	465.20	−13.256	284−399

in contrast to the "normal" temperature dependence of NQR frequencies, were $d\nu/dT$ is negative [13]. We shall discuss this point later.

Only one more transition frequency, ν_3, was observed in the ^{127}I NQR spectra of the title compounds. We assign ν_3 to a transition $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ of the terminal iodine atoms (A). ν_3 increases from 67.19 MHz ($M^{3\oplus} = Dy$) to 76.65 MHz ($M^{3\oplus} = Yb$), see Table 3. In the case of $Cs_3Dy_2I_9$ for which ν_3 is fairly low, temperature dependent measurements show positive temperature coefficients as the atom (B) do. ν_4 we could not measure because of the limited frequency range of our instrument.

Each of the cesium-tri-μ-iodohexaiododimetallates (III) studied experiences a phase transition below room temperature. The phase transition temperatures T_{tr} decrease from M = Dy to M = Yb, $Cs_3Yb_2I_9$ having T_{tr} slightly below 77 K. We observed the phase transition of the latter compound by the decrease of the signal to noise ratio, S/N, at 77 K. In Table 5 the T_{tr} are given together with the ionic radii of the $M^{3\oplus}$ ($RE^{3\oplus}$) recommended by Shannon and Prewitt [14]. For all compounds studied, S/N is significantly de-

Table 5. Phase transition temperatures T_{tr} of the cesium enneaiododimetallates(III) examined, and their ionic radius $r(RE^{3\oplus})$ [14].

Substance	T_{tr}/K	$r(RE^{3\oplus})$/pm
$Cs_3Dy_2I_9$	251	90.8
$Cs_3Y_2I_9$	247	90.0
$Cs_3Ho_2I_9$	212	89.4
$Cs_3Er_2I_9$	155	88.1
$Cs_3Yb_2I_9$	<77	85.4
$Cs_3Tb_2I_9$	118	92.3
$Cs_3Sm_2I_9$	231	96.4
$Cs_3Nd_2I_9$	<284	99.5

Table 6. The asymmetry parameter $\eta(^{127}\mathrm{I})$ and the nuclear quadrupole coupling constant $e\Phi_{zz}Qh^{-1}(^{127}\mathrm{I})$ at room temperature of the measured cesium enneaiododimetallates(III) (* different temperature).

Substance	Transition $\nu_1 \rightarrow \nu_2$		Transition $\nu_3 \rightarrow \nu_4$		$r(\mathrm{RE}^{3\oplus})$/ pm
	η/%	$e\Phi_{zz}Qh^{-1}$/ MHz	η/%	$e\Phi_{zz}h^{-1}$/ MHz	
$Cs_3Dy_2I_9$	1.9	135.18	–	–	90.8
$Cs_3Y_2I_9$	0.0	141.82	–	–	90.0
$Cs_3Ho_2I_9$	0.0	144.33	–	–	89.4
$Cs_3Er_2I_9$	0.0	154.59	–	–	88.1
$Cs_3Yb_2I_9$	0.0	174.86	–	–	85.4
$Cs_3Tb_2I_9$	80.5	152.40	62.7	269.94	92.3
$Cs_3Sm_2I_9$	79.0	138.71	52.8	244.29	96.4
$Cs_3Nd_2I_9$	91.8	127.07	83.0	208.63	99.5
$Cs_3Pr_2I_9$	100.0	123.11 *	100.0	178.39 *	101.3

creased below T_{tr} and only ν_1 could be detected. About 40 K below T_{tr}, ν_1 fades out, too, and no signal was detected in the range 10 MHz to 60 MHz.

From the two ^{127}I NQR frequencies ν_1 and ν_2, for the bridging atoms B the asymmetry parameter $\eta(^{127}\mathrm{I})$ of the electric field gradient tensor, EFGT, $\eta = |\Phi_{xx} - \Phi_{yy}|/|\Phi_{zz}|$, and the nuclear quadrupole coupling constant (NQCC) $e\Phi_{zz}Qh^{-1}$ can be calculated following the equations given in [15]. Φ_{zz} is the main principal axis of the EFGT, e the unit charge, Q the nuclear electric quadrupole moment and h the Plancks constant. The calculated values of $e\Phi_{zz}Qh^{-1}(^{127}\mathrm{I})$ and $\eta(^{127}\mathrm{I})$ are listed in Table 6. In Fig. 4 the temperature dependence of $e\Phi_{zz}Qh^{-1}(^{127}\mathrm{I})$ is plotted. We shall mention an interesting point. In Table 6 one finds that the asymmetry parameters of the bridging atoms in the title compounds are very low, nearly zero. This is a rather surprising observation. The point symmetry of the bridging atoms B in the hexagonal cell is mm and therefore $\eta(^{127}\mathrm{I})$ should be unequal zero. On the basis of our present experimental data we must assume that the EFGT at the B-site is nearly rotational symmetric due to the coordination of the B-atoms.

Cesium enneaiodometallates(III), $Cs_3M_2I_9$, with $M = Tb, Sm, Nd, Pr$

From the ^{127}I and from the X-ray powder diffraction pattern it is evident that this group of title compounds crystallizes with a structure type different from the $Cs_3Cr_2Cl_9$-type. For each compound we find four ^{127}I NQR lines, except the M = Pr compound for which we have observed two NQR frequencies only. On $Cs_3Gd_2I_9$ we failed to observe an NQR spectrum, the reason for this being not clear yet.

According to four resonance lines there must be two crystallographically independent iodine atoms in the unit cell. The first one shows the transition frequencies in the range $31.79 \leq \nu_1(^{127}\mathrm{I})/\mathrm{MHz} \leq 35.30$ and $34.06 \leq \nu_2(^{127}\mathrm{I})/\mathrm{MHz} \leq 41.62$. The spectra of the second iodine atom are found within $46.40 \leq \nu_3(^{127}\mathrm{I}) \leq 55.03$ and $56.74 \leq \nu_4(^{127}\mathrm{I})/\mathrm{MHz} \leq 75.96$. In Table 3 the frequencies observed at room temperature are listed. $\eta(^{127}\mathrm{I})$ and $e\Phi_{zz}Qh^{-1}(^{127}\mathrm{I})$ were calculated with the aid of the equations given in [15]; the results are listed in Table 6.

The temperature dependence of the ^{127}I NQR for the enneaiodides with M = Tb, Sm, Nd, is more complex then that of the group with $Cs_3Cr_2Cl_9$-type structure (see Figure 5). The three compounds undergo a phase transition (see Table 5), which was not observed in the DTA experiment. The curves $\nu(^{127}\mathrm{I}) = f(T)$ have been parameterized according to the temperature coefficients $\mathrm{d}\nu(^{127}\mathrm{I})/\mathrm{d}T$ of the three compounds M = Tb, Sm, Nd, within the group and also with the coefficients of the $Cs_3Cr_2Cl_9$-type cesium enneaiodides of the rare earths. $\nu_1(^{127}\mathrm{I})$ is nearly temperature independent above $T = T_{tr}$ and slightly positive below T_{tr}. ν_2 shows normal Bayer behavior with rather large $\mathrm{d}\nu/\mathrm{d}T$ below $T = T_{tr}$ and small $\mathrm{d}\nu/\mathrm{d}T$ above T_{tr}. The $\nu_3(^{127}\mathrm{I})$ are in their temperature behavior very similar to the ν_1 of the Cs_3Cr_2Cl-type enneaiodides: A nearly constant, positive temperature coefficient of the NQR frequencies above T_{tr} and slightly changing temperature coefficients below T_{tr} (compare Figures 3 and 5).

Discussion

The governing feature of all rare earth halogenide complexes studied here is the ionic radius $r(\mathrm{RE}^{3\oplus})$. There is a rather dense packing of $\mathrm{Cs}^{\oplus}$ and $\mathrm{I}^{\ominus}$ in the $Cs_3Cr_2Cl_9$-type structure, and the rare earth ions $\mathrm{RE}^{3\oplus}$ are enclosed within the octahedral holes of the halogen packing. Closed packed layers CsI_3 (Fig. 6) are stacked along the crystallographic c-axis in the arrangement A, B, A, C, B, C, … (see Figure 7). A, B, C are the three different stacking positions of a CsI_3 layer. Between this layer arrangement the iodines form octahedral holes. Two thirds of these interstitial sites are occupied by $\mathrm{RE}^{3\oplus}$ in such a way that face sharing octahedra $\mathrm{RE}^{3\oplus}\mathrm{I}_6$ are formed, having 3/m symmetry. The three bridging halogens belong to the layer B which is the mirror plane *m* in $c/4$ of the hexagonal axis, and the six terminal iodines of the double octahedron $[I_3RE(I_3)_BREI_3]^{3\ominus}$ are located in the A and C layer, respectively.

The high stability of $Cs_3M_2I_9$ can be understood. On exchanging the cation $Cs^{\oplus}$ against a smaller one, for example against $Rb^{\oplus}$, the AI_3 layer becomes instable because of the differing radii of $Rb^{\oplus}$ and $I^{\ominus}$, respectively. The exchange of iodine against bromine or chlorine leads to a diminuation of the octahedral interstitial sites and the ions $RE^{3\oplus}$ become to large to fit into these interstitial sites. Therefore such compounds are less stable. If they exist, they melt incongruently.

A metal-metal bond between two neighboring $M^{3\oplus}$, as it is discussed in enneahalogenodimetallates with M = Zr, Mo, W [2, 16], must not be considered for $M = RE^{3\oplus}$. This can be seen from the c/a-ratios of the title compounds. The bi-octahedral units are oriented along [001]. If there is some attraction between two neighbouring metal centers of the unit $[RE_2I_9]$, it causes a shortening of the *c*-axis and a compound with a metal-metal interaction within the bi-octahedron should show a c/a-ratio ≤ 2.41. c/a in the title compounds is ≥ 2.52 (see Table 2), an indication for Coulomb repulsion of the ions $RE^{3\oplus}$ [2].

The largest cation fitting into the octahedral interstitials without disturbing the crystal structure is the ion $Dy^{3\oplus}$. If we consider the $I^{\ominus}$-ions as hard spheres with the radius $r(I^{\ominus}) = 220$ pm, the octahedral interstitial sites have a radius of $r = 91.1$ pm. This is a very little larger than $r(Dy^{3\oplus}) = 90.8$ pm (see Table 5). The ^{127}I NQR spectra and the X-ray powder diffraction results show that all compounds $Cs_3M_2I_9$ with $r(M) > r(Dy^{3\oplus})$ have a crystal structure differing from that of the $Cs_3Cr_2Cl_9$-type. Their asymmetry parameters $\eta(^{127}I)$ are large and the $\nu(^{127}I) = f(T)$ curves do not have a constant positive slope.

An interesting question can be raised: What happens with the nuclear quadrupole coupling constant (NQCC) and hence with the EFG when the rare earth ion varies? From the X-ray data we found that the lattice constants are almost not changing with variation of $RE^{3\oplus}$, as long as we stay within the $Cs_3Cr_2Cl_9$-type, $P6_3/mmc\text{-}D^4_{6h}$. Therefore, the distance $d(RE-I)$ should not vary with variation of $r(RE^{3\oplus})$. One of the reasons, why the EFG (the NQCC) increases with decreasing $r(RE^{3\oplus})$ may be a stronger polarization of the $I^{\ominus}$-ion by smaller cations $M^{3\oplus}$. Table 6 shows this dependence clearly. In Fig. 8, $e\Phi_{zz}Qh^{-1}(^{127}I) \equiv e^2qQh^{-1}(^{127}I)$ is plotted as a function of $r(RE^{3\oplus})$. For the $Cs_3Cr_2Cl_9$-type enneaiododimetallates(III) there is a linear decrease of $e^2qQh^{-1}(^{127}I)$ with increasing $r(RE^{3\oplus})$ for the B atoms. For the non-$Cs_3Cr_2Cl_9$-type compounds the decrease of $e^2qQh^{-1}(^{127}I)$ with increasing $r(RE^{3\oplus})$ is clearly seen. The deviations from linearity are slight for both crystallographic sites of iodine.

Interesting is also the linear dependence of the phase transition temperature T_{tr} on the rare earth radius $r(RE^{3\oplus})$ within the group of $Cs_3Cr_2Cl_9$-type cesium enneaiododimetallates(III). We find

$$T_{tr}/K = -2974 + 35.62\,r(RE^{3\oplus})/pm\,. \qquad (2)$$

The functions graphically given in Figure 9. It may well be that the phase transition is due to a locking of the rare earth ion, vibration in a symmetrical manner within the interstitial site in the high temperature phase I, to an unsymmetric position within the cage in phase II. A smaller cation may need less activation energy than a larger one to move from the potential minimum at the unsymmetric position to the minimum of the symmetric position. Therefore, the transition temperature is proportional to $r(RE^{3\oplus})$.

To discuss the temperature behavior of the ^{127}I NQR of the $Cs_3Cr_2Cl_9$-type cesium enneaiododimetallates(III), we follow the theory Haas and Marram [17] have developed to explain positive (anti-Bayer) temperature coefficients of halogen NQR in halogeno complexes of 5d metals.

The "normal" temperature behavior of NQR spectra was first discussed by Bayer [13]. He considers single bonds with σ-character only. It is assumed that the stretching vibrations are in the ground state and not influenced by the variation of temperature. With increasing temperature the librational motions increase, whereby the EFG at the site of the nucleus considered is decreasing. As a consequence, the NQR frequencies decrease, too. The situation changes if one considers halogen atoms bonded to transition metals. Here the low energy vibrations also decrease the EFG with increasing temperature. But additionally, if the central metal ion has unoccupied d-orbitals with an orientation effective to the t_{2g} states and if the coordination of the halogen ions around the central metal ion is an octahedral one, it is possible that electron density migrates from the p_x and p_y halogenide orbitals into the t_{2g} orbitals of the metal ion, thereby forming partial π-bonds. This diminuates the EFG at

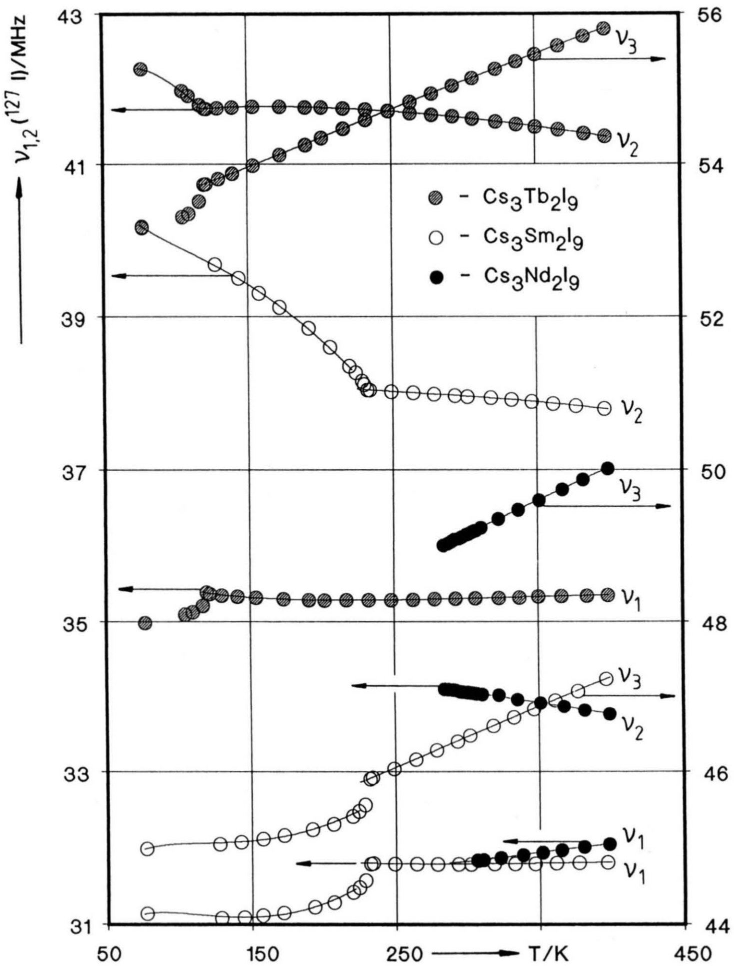

Fig. 5. $\nu_i(^{127}\text{I}) = f(T)$ of the cesium enneaiodometallates(III) with rare earth radius $r(\text{RE}^{3\oplus}) > r(\text{Dy}^{3\oplus})$.

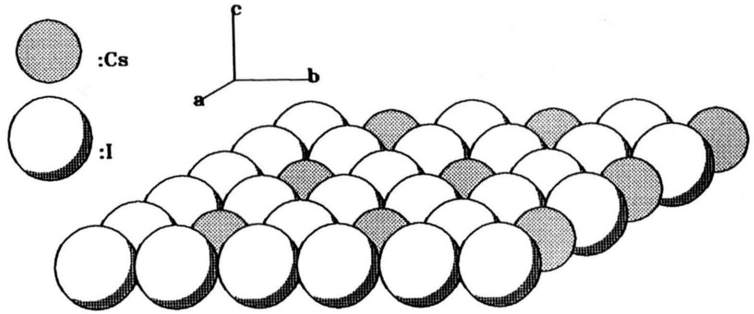

Fig. 6. Sketch of a single layer CsI_3.

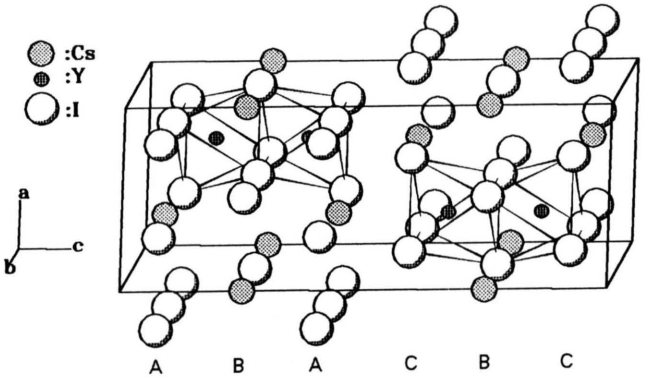

Fig. 7. The stacking sequence A, B, A, C, B, C, ... of the CsI_3 layers in the unit cell of $Cs_3Y_2I_9$ ($Cs_3Cr_2Cl_9$-type).

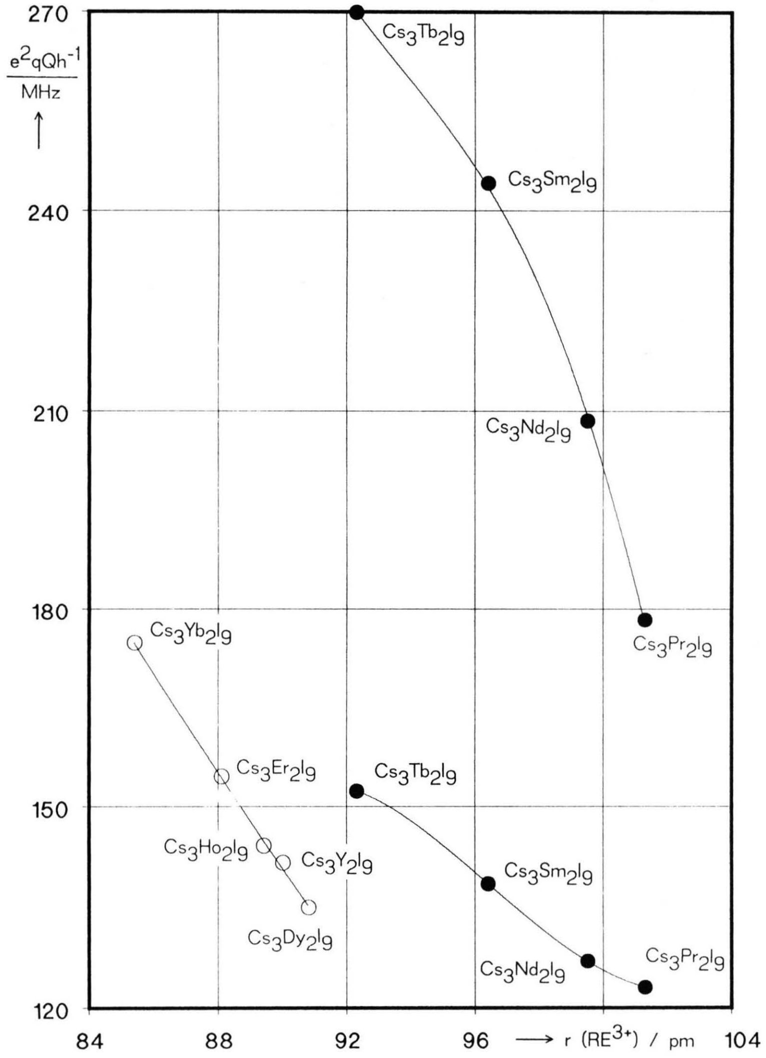

Fig. 8. The NQCC of ^{127}I as a function of the ionic radius of RE$^{3\oplus}$. The two structure types of the cesium enneaiododimetallates(III) are distinguished by ○ and ●.

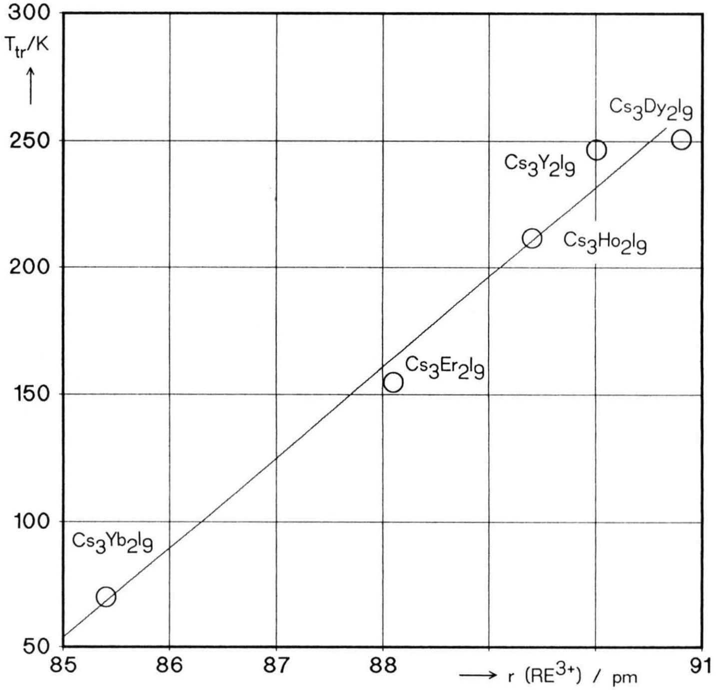

Fig. 9. Dependence of the phase transition temperature T_{tr} for cesium enneaiododimetallates(III) with $Cs_3Cr_2Cl_9$-type structure on the radius $r(RE^{3\oplus})$.

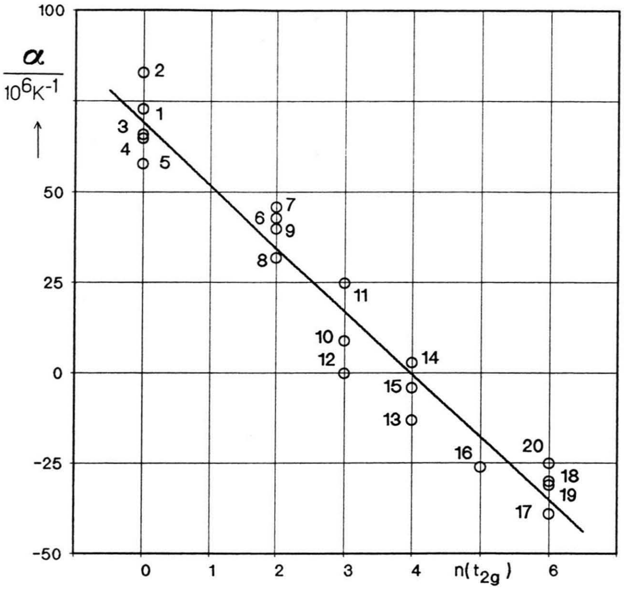

Fig. 10. Correlation between the relative temperature coefficient $\alpha = (\mathrm{d}\nu(^{127}\mathrm{I})/\mathrm{d}T)/\nu(^{127}\mathrm{I})$ as a function of the number n of electrons $n(\mathrm{t}_{2g})$ in the t_{2g} orbitals of the central transition metal ion (terminal halogen atoms only in octahedral and bi-octahedral complexes).

the halogen nucleus. Increasing temperature and increasing vibrational motions disturb the regular octahedral symmetry, which causes a weakening of the π-bond. The charge distribution on the site of the halogen becomes more p-character, the EFG and therefore the NQCC and the NQR resonance frequency increases.

This dependence of a $\pi \leftrightarrow$ p-bond character on temperature has been discussed by several authors [17–19] for the 5d elements in octahedral complexes A_2MX_6 (A = K, Rb, Cs; M = W, Re, Os, Ir, Pt; X = Cl, Br). They crystallize with cubic structures and octahedral coordination $MX_6^{2\ominus}$. In the present study it turns out that it is possible to compare the temperature behavior of the halogen NQR in octahedral complexes with a central metal atom $4f^x5d^0$ with the known NQR behavior of $5d^x$ central metal complexes. The lanthanides considered here have six vacancies in the t_{2g} orbitals, which may lead to a strong positive temperature coefficient of the ligand NQR.

Table 7. The relative temperature coefficient $\alpha = (\delta\nu/\delta T)/\nu$ of different compounds with regular and distorted octahedral halogen coordination around the central metal ion at room temperature. Z is the number of the data points in Figure 10. See also [19].

Compound	Z	$(\delta\nu/\delta T)/\nu \cdot 10^6$ K	Compound	Z	$(\delta\nu/\delta T)/\nu \cdot 10^6$ K
$Cs_3Dy_2I_9$ ν_3	1	73	Cs_2NaErI_6	4	66
Cs_2NaDyI_6	2	83	Cs_2NaYbI_6	5	58
Cs_2NaYI_6	3	65			
K_2WCl_6	6	43			
Rb_2WCl_6	7	46			
Cs_2WCl_6	8	32	Cs_2WBr_6	9	40
K_2ReCl_6	10	9	K_2ReBr_6	11	25
Cs_2ReCl_6	12	0			
K_2OsCl_6	13	−13	K_2OsBr_6	14	3
			Cs_2OsBr_6	15	−4
K_2IrCl_6	16	−26			
K_2PtCl_6	17	−39	K_2PtBr_6	18	−30
Cs_2PtCl_6	19	−31	Cs_2PtBr_6	20	−25
$Cs_3Dy_2I_9$ ν_1		371	ν_2		376
$Cs_3Y_2I_9$ ν_1		348	ν_2		349
$Cs_3Ho_2I_9$ ν_1		356	ν_2		350
$Cs_3Er_2I_9$ ν_1		304	ν_2		302
$Cs_3Yb_2I_9$ ν_1		241	ν_2		237

To compare the temperature coefficients measured here for several compounds, we calculated the relative temperature coefficient $\alpha = (\mathrm{d}\nu/\mathrm{d}T)/\nu$ at room temperature, and in Table 7 the α-values are listed for the title compounds, including transition metal complexes from literature. In Fig. 10 the coefficients α (at room temperature) are plotted against the number n of electrons in the t_{2g} orbitals for several cubic hexahalogenometallates(IV) with 5d metals and the present 4f metals. The temperature coefficients of the ^{127}I NQR frequencies observed correlate well with the literature data for halogen ions in $5d^x$ complexes. Also α for some iodo elpasolithes Cs_2NaREI_6 [20]

with regular octahedral arrangement of the iodines around ($RE^{3\oplus}$) is included. The correlation is valid only for the terminal halogens. The temperature coefficient α of the bridging atoms is, due to the two metal centers they belong to, much higher (see Table 7).

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