^{35}Cl NQR of Impurity Molecules of Tetrachlorides of Group IV Elements in Matrix Crystals of Group IV Element Halides

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^{35}Cl NQR spectra of the impurity molecules $E'Cl_4$ (1.5–5% mol) (E' = C, Si, Ge, Sn) in the matrix crystals of Group IV tetrachlorides ECl_4 (E = Si, Ge, Sn, Ti) have been measured at 77 K. The mixtures of the above components are substitution solid solutions. Changes in the ^{35}Cl NQR spectra of the impurity molecules have been analysed as to packing factors and nearest environment.

Key words: NQR, ^{35}Cl, solid solutions, tetrachlorides of Group IV elements.

This work is a continuation of the studies described in [1], where the behavior of MBr_4 impurity molecules (M = C, Si, Ge, Ti, Sn) in matrix crystals of tetrachlorides and tetrabromides of Group IV elements was studied. However, the field constants for the bromine atom in these compounds are subject to essential changes, which should not be the case in the chlorine containing molecules. Therefore all experiments in this work were carried out on chlorine containing molecules: molecules $E'Cl_4$ (E' = C, Si, Ge, Sn) were used as impurities in matrix crystals of tetrachlorides of Group IV elements.

Experimental

All specimens were obtained by mixing the components and subsequent quenching in liquid nitrogen, as done before [1, 2]. The concentration of the impurity molecules was 1.5–5% mol. The ^{35}Cl NQR spectra were measured on a pulse NQR spectrometer ISSh-2-13 at 77 K. The accuracy in the frequency measurements was ≈ 3 kHz.

The incorporation of the impurity molecules was recognized by the appearance of the "impurity" satellite lines in the NQR spectra of the matrix crystals, see [1].

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Results and Discussion

Results of measurements are presented in Table 1. One can see that, according to the structure of the matrix crystals (The crystals used as tetrachloride matrixes are monoclinic, space group $P2_1/c$, $Z = 4$), with molecules in general positions. The latter corresponds to a quadruplet NQR spectrum for chlorine.) [1, 3], all the ^{35}Cl NQR spectra of the impurity molecules are quadruplets. A schematic view of the ^{35}Cl NQR spec-

Table 1. ^{35}Cl NQR spectra of the impurity molecules of tetrachlorides of Group IV elements in matrix crystals at 77 K (frequencies in MHz).

Lattice	Impurity			
	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
$SiCl_4$	40.728	20.273	25.459	23.708
	40.875	20.408	25.670	23.984
	40.893	20.415	25.690	24.020
	40.980	20.464	25.703	24.027
$GeCl_4$	40.687	20.300	25.450	23.693
	40.883	20.443	25.715	24.031
	40.894	20.460	25.735	24.081
	41.005	20.508	25.745	24.091
$SnCl_4$	40.650	20.380	25.490	23.720
	40.928	20.520	25.838	24.140
	40.942	20.570	25.855	24.226
	41.058	20.600	25.879	24.296
$TiCl_4$	40.777	20.406	25.569	23.815
	40.928	20.506	25.776	24.099
	40.949	20.514	25.806	24.127
	41.032	20.550	25.813	24.213

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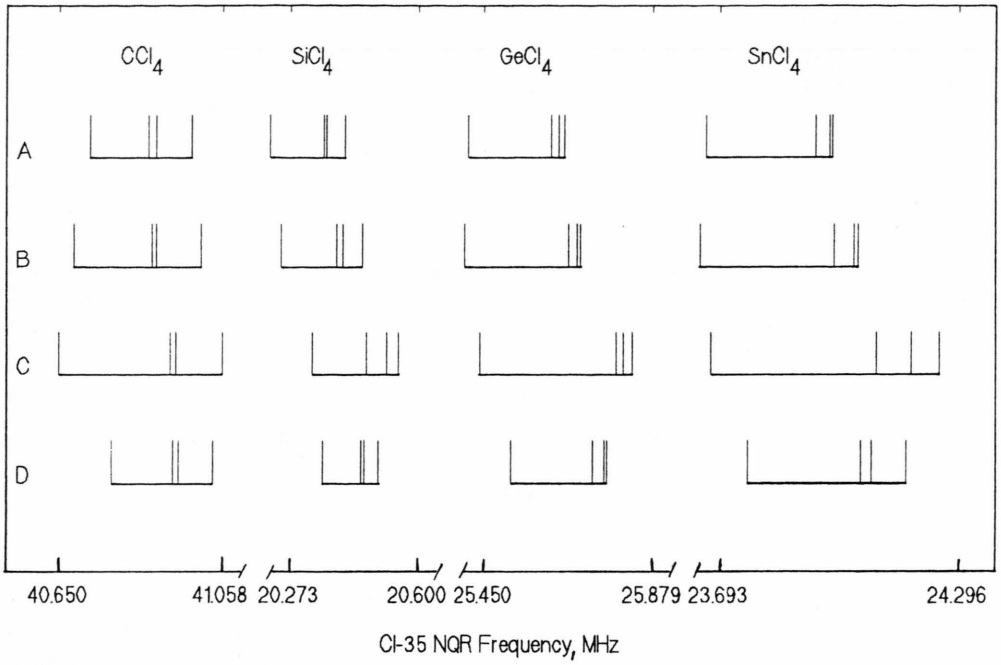

Fig. 1. ^{35}Cl NQR spectra of the impurity molecules of tetrachlorides of non-transitional group IV elements in matrix crystals of tetrachlorides of group IV elements. Matrix crystal lattices (per line): A – $SiCl_4$, B – $GeCl_4$, C – $SnCl_4$, D – $TiCl_4$.

tra of the impurity molecules for the whole series of specimens under study is shown in Figure 1. There are shifts of the frequency line centers, changes in the mutual positions of spectral lines and values of the frequency splittings between the spectral components as compared to the spectra in their own lattices. For the carbon tetrachloride impurity the alien matrix imposes another symmetry of the crystalline environment on the CCl_4 molecules. Changes in the multiplicity of the NQR spectrum of impurity molecules and in the intensity ratios of their components also occur (see Figure 2).

For a further interpretation of the experiments the ^{35}Cl spectral components of the impurity molecules were divided into two groups. Each of them was considered separately. The first group included the high frequency triplet lines (ν_2–ν_4), the second group consisted of a single low frequency line (ν_1). For the whole series of matrix lattices the observed changes in the average frequency of the high frequency triplet ($\bar{\nu}$) was assumed to be dependent on the volume factor; changes in the low frequency line might be due to weak coordination interactions [1, 3].

Actually, with the exception of the titanium tetrachloride matrix point, there is a good correlation between the $\bar{\nu}$ values of the impurity molecules and their formal close packing coefficients (K) in the matrix crystal lattices

$$\bar{\nu} = [\nu_0 + b \cdot K] \pm \delta \,. \tag{1}$$

The K-values used in deriving (1) are listed in Table 2; the parameters of (1) for the impurity molecules in the silicon, germanium and tin tetrachloride lattices are listed in Table 3. We assume that ν_0 in (1) represents the frequency of the impurity molecule at $K \to 0$, i.e. in the gas case.

In fact, the magnitudes of shifts for the impurity molecules (2.2, 5.5, 5.4, and 6.5% for C, Si, Ge, and Sn, respectively), when compared with the frequencies observed in their own lattices, are characteristic of the

Table 2. Values of the formal close packing coefficients K.

Lattice	Impurity			
	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
$SiCl_4$	0.654	0.715	0.740	0.805
$GeCl_4$	0.632	0.691	0.715	0.778
$TiCl_4$	0.630	0.689	0.713	0.775
$SnCl_4$	0.581	0.635	0.657	0.715

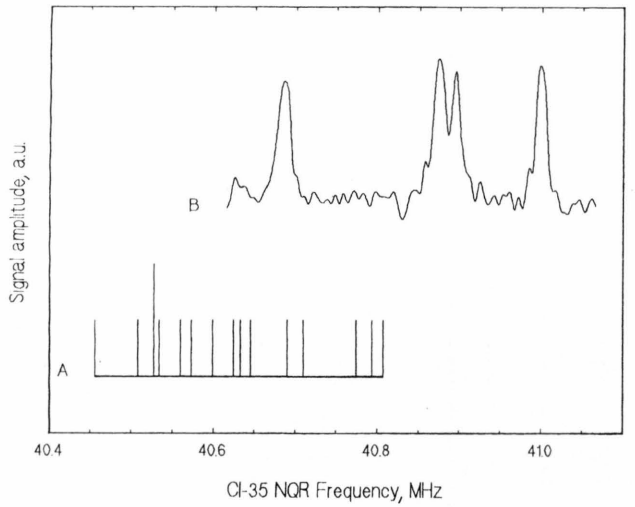

Fig. 2. ^{35}Cl NQR spectra of carbon tetrachloride: A) in its own crystal lattice; B) the impurity of 2.1% mol. of CCl_4 in the $GeCl_4$ matrix crystal lattice.

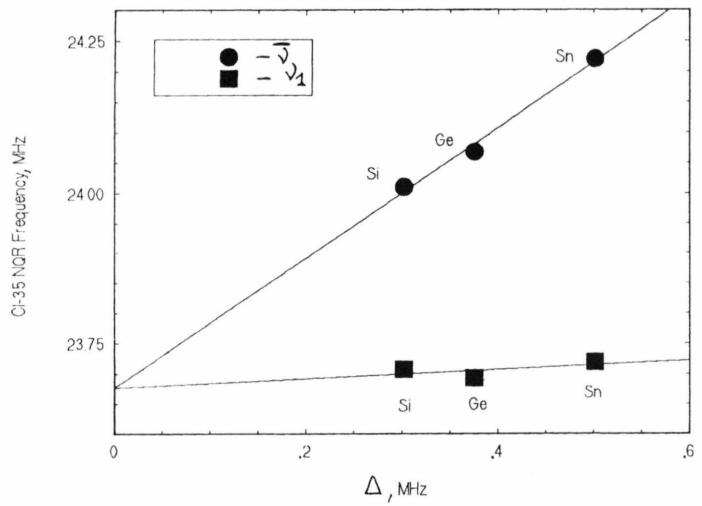

Fig. 3. Relation between the ^{35}Cl NQR frequencies of the $SnCl_4$ impurity molecules and their difference $\Delta = \bar{\nu} - \nu_1$.

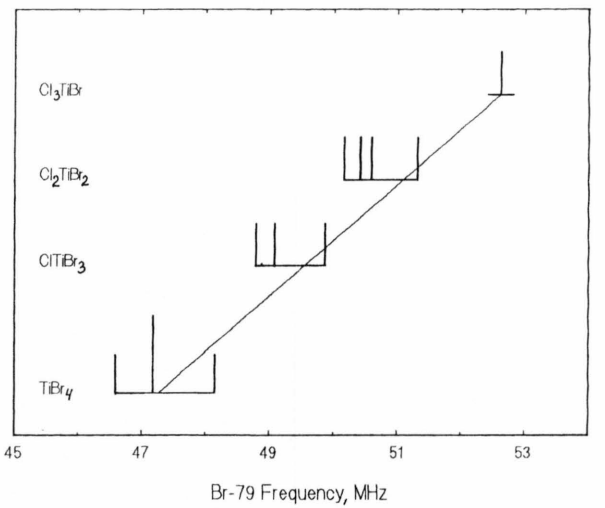

Fig. 4. Schematic view of ^{79}Br NQR spectra of Cl_nTiBr_{4-n} ($n = 0 \ldots 3$) compounds at 77 K.

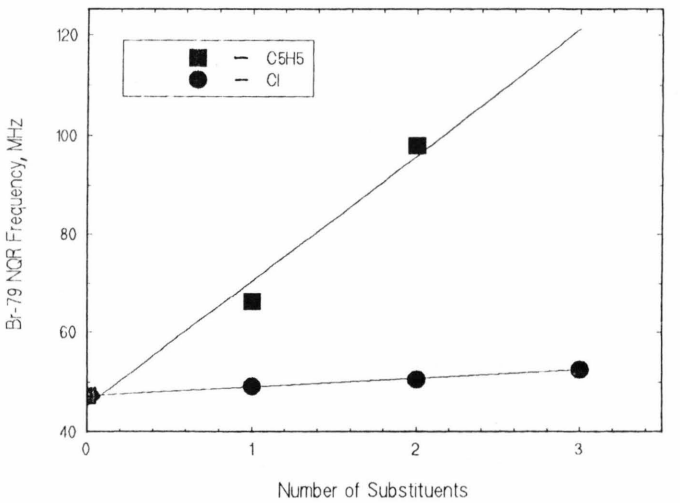

Fig. 5. Dependence of average ^{79}Br NQR frequencies of $(R)_nTiBr_{4-n}$ compounds (R = Cl, C_5H_5) on the number of substituents R.

"so called" solid state shifts of the NQR frequencies [4].

It is noteworthy that the points for the titanium tetrachloride matrix lattice do not follow the dependence (1), but are fairly well described by the dependence

$$\bar{\nu}(E'Cl_4) = \nu_0 + c \cdot \bar{\nu}(SiCl_4) \quad (2)$$

if one uses ^{35}Cl NQR $\bar{\nu}$ frequencies of $SiCl_4$ in the crystalline lattices of silicon, germanium, titanium and tin tetrachlorides.

Dependences like (2) are not observed for the low frequency lines except $\nu_1(SnCl_4) = F[\nu_1(GeCl_4)]$:

$$\nu_1(SnCl_4) = [-1.929 + 1.007 \cdot \nu_1(GeCl_4)] \pm 0.006; \quad n = 4;\ r = 0.99. \quad (3)$$

The sequence order of matrix crystals is also changed: it becomes $Ge < Si < Sn \ll Ti$ instead of $Si < Ge < Ti < Sn$.

The abnormal spectral behavior of the impurity molecules in the titanium chloride lattice confirms the existence of weak coordination interactions (see [1]). Since titanium is a transition element, coordination interactions between chlorine atoms, corresponding to ν_1, and titanium are of a different nature than those between the central atoms of non-transition elements Silicon, Germanium and Tin. This is confirmed when comparing changes in the $\bar{\nu}$ and ν_1 frequencies with their difference $\Delta = \bar{\nu} - \nu_1$ (see Figure 3)

$$\nu = [\nu_0 + (a \mp 0.5) \cdot \Delta] \pm \delta\,. \quad (4)$$

Parameters of equation (4) are listed in Table 4 (for the calculation of $\bar{\nu}$ values $(a - 0.5)$ is taken, otherwise for ν_1).

When studying the mixtures of $TiBr_4$ with $GeCl_4$ we came across a specific case of exchange between the two compounds. We managed to observe the ^{79}Br NQR spectra for Cl_nTiBr_{4-n} compounds (see Table 5 and Figure 4). Changes in the average NQR frequencies (ν_{av}) for the bromine atoms in these compounds are described by a linear dependence

$$\nu_{av} = \nu_0 + d \cdot N_{Cl}\,, \quad (5)$$

Table 3. Parameters of (1) for $E'Cl_4$ in the matrix crystals lattices.

E′	ν_0	b	δ	n	r
C	41.464	−0.843	0.004	3	0.992
Si	21.622	−1.669	0.004	3	0.999
Ge	27.707	−2.057	0.004	3	0.999
Sn	25.902	−2.352	0.003	3	0.999

Table 4. Parameters of (4) for the $E'Cl_4$ impurity molecules in matrix crystals lattices.

E′	ν_0	a	δ	n
C	40.827	−0.052	0.007	3
Si	19.650	4.437	0.016	3
Ge	25.394	0.748	0.012	3
Sn	23.677	0.577	0.011	3

Table 5. ^{79}Br NQR spectra in Cl_nTiBr_{4-n} and $(Cp)_nTiBr_{4-n}$ compounds at 77 K.

^{79}Br NQR frequency, MHz			
$TiBr_4$	$ClTiBr_3$	Cl_2TiBr_2	Cl_3TiBr
46.58	48.78	50.15	52.62
47.17	49.07	50.40	
47.17	49.86	50.58	
48.14		51.30	
$TiBr_4$	$CpTiBr_3$	Cp_2TiBr_2	Cp_3TiBr
46.58	66.011	96.33	
47.17	66.231	97.58	–
47.17	66.704	97.81	
48.14		100.00	

where N_{Cl} is the number of chlorine atoms in the molecule. Comparing the observed changes with analogous ones in the $(C_5H_5)_nTiBr_{4-n}$ [5] compounds we found that the π-electron donor ability for the chlorine atoms is considerably smaller than that for π-cyclopentadienyl substituents (see Table 5 and Figure 5)*.

* All NQR spectra of pure tetrachlorides were taken from the book by G. K. Semin, T. A. Babushkina, and G. G. Yakobson, "NQR in Chemistry"/J. Wiley & Sons, New York 1975.

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