X-Ray, NMR, and NQR Investigations of the Crystal Structure and Charge Distribution of Sodium Tetrachloroaluminate, $NaAlCl_4$

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On single crystals of $NaAlCl_4$ the NMR- and NQR-spectra of ^{23}Na, ^{27}Al, and ^{35}Cl were studied at room temperature. The crystal structure of $NaAlCl_4$ has been refined. A comparison of the NMR (NQR) data with the crystal structure data shows that the electric field gradients (EFG) at the chlorine sites are mainly determined by the partial covalency of the Al-Cl bond, whereas the EFG at the aluminum sites is determined by the small deviations of the $AlCl_4^{\ominus}$ ion from tetrahedral symmetry and by the influence of the lattice. $|e^2 q Q/h|$ (^{23}Na) proves the dominant ionic character of sodium in the lattice. The experimental results for the crystal structure show minor deviations from Baenziger's data.

The NMR (NQR) data at $T = 22$ °C are [atom ($|e^2 q Q/h| / \mathrm{MHz}$; η)]: ^{23}Na (1.1117 ± 0.0012; 0.2153 ± 0.0005); ^{27}Al (1.4895 ± 0.0012; 0.3375 ± 0.0011); $^{35}Cl_{I}$ (23.033 ± 0.030; 0.182 ± 0.025); $^{35}Cl_{II}$ (22.520 ± 0.010; 0.270 ± 0.005); $^{35}Cl_{III}$ (21.646 ± 0.003; 0.315 ± 0.007); $^{35}Cl_{IV}$ (22.410 ± 0.016; 0.197 ± 0.010).

I. Introduction

The nuclear quadrupole interaction of an atomic nucleus in a solid depends on its nuclear electric quadrupole moment eQ and on the electric field gradient tensor $\mathbf{V}$ created by the electric charges around the nucleus. Thus it is a function of the electric charge distribution $\varrho(x, y, z)$ within the solid. Studies of the nuclear quadrupole interactions may therefore provide an understanding of the nature of the chemical bond in solids. Single crystal experiments are preferable because the nuclear quadrupole interaction is a tensor property and thereby complete information can be obtained. NMR and NQR investigations are a convenient experimental basis to study nuclear quadrupole interactions in solids.

The results of single crystal studies of "ionic" solids are often interpreted within the framework of a simple point charge model or an extended point charge model, the latter one including also the influence of electric multipole moments on the electric field gradient. A rather ideal situation is present if each element of which the lattice is composed contains an isotope with a nuclear quadrupole moment unequal zero. In addition, the isotopic abundance should be high to make the NMR (NQR) experiment not too difficult. In such a case one should be able to test the charge distribution model quite satisfactorily.

Sodium tetrachloroaluminate, $NaAlCl_4$, is a compound which satisfies the condition to be a "total spin system". Each of the natural abundant nuclei (^{23}Na, ^{27}Al, ^{35}Cl, ^{37}Cl) has an electric nuclear quadrupole moment and the abundance of these nuclei is high. Therefore, this substance seemed to be a good example to test the extended point charge model. For a chemically similar system, $NaBF_4$, a combined X-ray and NMR (NQR) study was done a few years ago[1].

To deduce a model for the charge distribution from a study of the nuclear quadrupole interactions in solids it is necessary to know the crystal structure. Therefore, our NMR and NQR studies have been accompanied by a refinement of the known crystal structure of $NaAlCl_4$, which was determined some time ago by Baenziger[2].

II. Experimental

1. Crystal Growth

Large single crystals had to be produced for the NMR experiments. The crystals were grown by a zone melting method. The phase diagram of the system NaCl-$AlCl_3$ has been investigated and described by several authors[3–5]. According to the work of Kendall et al.[3], Chrétien and Lous[4], and Fischer and Simon[5], the stoichiometric compound $NaAlCl_4$ melts dystectically at $T \approx 152$ °C. The solidus curve rises steeply with very small concentrations of NaCl above 50 at% towards the melting

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point of NaCl (803 °C). In the phase diagram at 50.5 mole% NaCl an eutectic point is present.

$NaAlCl_4$ was prepared by melting a mixture of pure anhydrous aluminium chloride and reagent grade sodium chloride within an evacuated glass apparatus at $T \approx 180$ °C. The sodium chloride was in slight excess to the stoichiometric ratio (1:1). Because of the steep rise of the solidus curve near 50 mole% $AlCl_3$, the resulting melt had nearly the wanted composition at this temperature. The melt was poured within the closed system into a glass ampoule where it crystallized. The polycrystalline solid $NaAlCl_4$ was then put into a teflon boat (width = 40 mm, length = 320 mm), which was placed into a glass tube. This procedure was done within a glove box which had been carefully dried with P_2O_5. The glass tube containing the teflon boat and the substance was evacuated and sealed. Then the boat was brought into a horizontal zone melting apparatus and the sample was purified by zone melting. When the substance had passed the melting zone about five times, single crystals of several cm length grew from the melt (crystallization speed = 0.2 mm/h). Well developed single crystals of 1 to 2 cm^3 size have been obtained in this way [6, 7].

The single crystals were isolated, transferred into glass cylinders, and sealed therein with polyester resin. A filling factor of 0.5 ... 0.7 was reached within the oscillator coil by this method. In some cases the crystals were doped during the growth with about 0.1% Fe^{3+} ions to lower the relaxation time during the NMR experiments ($NaFeCl_4$ is isomorphous to $NaAlCl_4$ [8]). For the X-ray work samples free of iron were used.

2. *X-Ray Investigations*

The lattice constants of $NaAlCl_4$ were determined by the Debye-Scherrer-Guinier powder technique. For the refinement of the crystal structure an automatic two circle X-ray diffractometer (Stoe) was used. The data were collected on the basis of the Weissenberg equi-inclination method with monochromatic (LiF) CuKα-radiation. The crystal was a small prism of irregular shape with an approximately triangular cross section of ca. 0.4 mm mean diameter, [100] extending in the direction of the prism axis. The diffractometer was run in the ω scan. Eleven layers $(h\,k\,l)$, $h = 0, \dots, 10$ were taken with [100] as the rotation axis. Appropriate corrections for the Lorentz-polarization factor and the absorption were applied.

3. *NMR and NQR Experiments*

The NMR spectra of ^{23}Na and ^{27}Al in $NaAlCl_4$ were investigated by taking rotation diagrams. The three main crystal axes [100], [010], and [001] were used in turn as the rotation axes, which are perpendicular to the external magnetic field $\boldsymbol{H}_0$. Fields H_0 in the range of 11 to 14 kOe were applied. The crystals, which were enclosed in glass envelopes, were affixed to a goniometer head and adjusted by means of Laue X-ray diffraction diagrams. They were transferred from the Laue camera to a one circle goniometer [9] which was fastened to the base of the magnet.

An error of ±1.5 angular degrees is the mean error in our X-ray and optical adjustment of [100], [010], and [001] perpendicular to $\boldsymbol{H}_0$. A further minimization of the error in the adjustment of the crystals was achieved by using the symmetry properties of the NMR spectrum. An overall angular error resulted which was well below 1 degree.

To study the NQR spectrum of ^{35}Cl in $NaAlCl_4$, the same geometrical set-up for the crystals was used. For all the NMR and NQR experiments at room temperature a wide line NMR spectrometer, Varian Type V 4200 B, has been used. Also the ^{35}Cl NQR Zeeman spectra were studied with the wide line spectrometer using magnetic fields of the magnitude $0 \leqq H_0 \leqq 200$ Oe. The pure NQR spectra at 77 K were recorded with the aid of a super-regenerative Dean-type NQR spectrometer. Single crystal NQR-Zeeman spectra were recorded by using the same magnet as for the wide line NMR spectra of ^{27}Al and ^{23}Na. The magnitudes of the small magnetic fields necessary for the Zeeman spectroscopy of ^{35}Cl in $NaAlCl_4$ were determined with the aid of a proton resonance meter and/or with a Hall probe. Using the remanent magnetization of the wide line magnet very stable fields in the order of 50 to 100 Oe were generated.

III. Results

1. *Crystal Structure Data*

From Guinier powder photographs the following lattice constants were determined at $T = (22 \pm 3)$ °C:

$$a = (10.331 \pm 0.002)\ \text{Å};$$
$$b = (9.905 \pm 0.002)\ \text{Å};$$
$$c = (6.189 \pm 0.001)\ \text{Å}.$$

Assuming 4 formula units within the unit cell, the density calculated from the X-ray data is: $\varrho_X = 2.011$ g/cm^3. This compares favorably with the pycnometric density $\varrho_{exp} = 2.013$ g/cm^3 as determined by Chrétien and Lous [4]. Baenziger [2] determined the lattice constants as: $a = 10.36$ Å, $b = 9.92$ Å, $c = 6.21$ Å; $\varrho_X = 1.996$ g/cm^3. Since $NaAlCl_4$

crystallizes with the space group $D_2^4 - P2_12_12_1$, all atoms occupy the general point position. Hence, 18 position parameters and 36 anisotropic temperature parameters had to be determined from the 514 independent reflections observed in the experiment. The absolute values of the experimental and calculated structure amplitudes were compared (the data are given in Table A). A weighted R-value of 0.079 is obtained.

The results of the least squares refinement are listed in Table 1. The improvement in the structure parameters due to the refinement is reasonable.

2. *Wide Line NMR Studies of ^{23}Na and ^{27}Al*

For the presentation of the experimental NMR results, we shall briefly introduce a few concepts. The magnetic field $\boldsymbol{H}_0$ was applied in turn perpendicular to the crystal axes [100], [010], and [001]. A system of axes x, y, z, connected with the electric field gradient tensor $\mathbf{V}$ is introduced. According to the crystal structure, this system may be different with respect to the crystal axes for each point position. A second coordinate system x', y', z', is determined by the external magnetic field $\boldsymbol{H}_0$, $\boldsymbol{H}_0$ and (z', y') are coplanar.

Finally, a third coordinate system x'', y'', z'', is defined by the main axes of the orthorhombic crystal system: $x'' \parallel [100]$; $y'' \parallel [010]$, $z'' \parallel [001]$. In Fig. 1 the coordinate systems and their interrelations are shown.

In the case of ^{23}Na and ^{27}Al, first order perturbation theory is sufficient to evaluate the nuclear quadrupole coupling constants from the experimental data. According to Volkoff et al.[10] the frequency splittings are determined by the relation

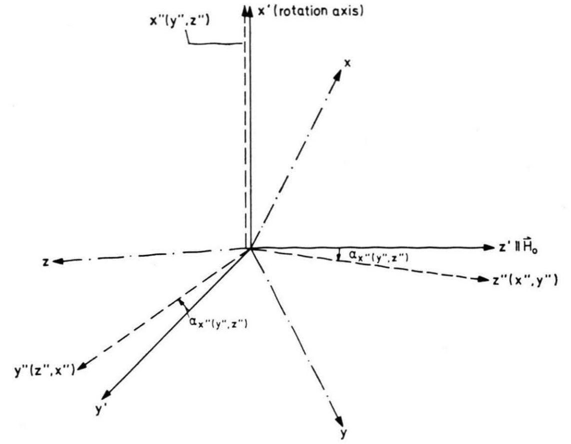

Fig. 1. The different coordinate systems used in this paper and their interrelations. x, y, z: main axes system of the NQ coupling tensor $\mathbf{V}$; x', y', z': coordinate system defined by the rotation axis $x' \perp \boldsymbol{H}_0$; x'', y'', z'': coordinate system correlated to the system of crystal axes ($x'' \parallel [100]$, $y'' \parallel [010]$, $z'' \parallel [001]$). For the crystallographic parameters the system $X = x''$, $Y = y''$, $Z = z''$, is used.

$$\Delta\nu_{x''} = |\nu_m - \nu_{-(m-1)}|_{x''} = A_{x''} + B_{x''} \cos 2\,\alpha_{x''} + C_{x''} \sin 2\,\alpha_{x''} \tag{1}$$

where $\alpha_{x''}$ is the rotation angle in the plane (y'', z'') with respect to the rotation axis x''. The phase of this angle $\alpha_{x''}$ is fixed by the constant $A_{x''}$. The coefficients of Eq. (1) are defined by the relations:

$$A_{x''} = \tfrac{1}{2} K (V_{y''y''} + V_{z''z''}) = -\tfrac{1}{2} K\, V_{x''x''}\,, \tag{2}$$

$$B_{x''} = \tfrac{1}{2} K (V_{y''y''} - V_{z''z''})\,, \tag{3}$$

$$C_{x''} = -K \cdot V_{y''z''}\,, \tag{4}$$

Table 1. Position parameters and anisotropic temperature factors for $NaAlCl_4$ as determined by the crystal structure refinement. The parameters found by Baenziger[2] are given in brackets.

Coordinate	Atom					
	Na	Al	Cl_I	Cl_{II}	Cl_{III}	Cl_{IV}
X	0.1251 (17) [0.128 (10)]	0.0380 (7) [0.039 (30)]	0.0320 (7) [0.031 (20)]	0.1481 (7) [0.148 (10)]	0.3469 (6) [0.348 (10)]	0.3773 (7) [0.379 (20)]
Y	0.2116 (11) [0.207 (<10)]	0.4857 (7) [0.485 (30)]	0.4919 (6) [0.490 (<10)]	0.3153 (4) [0.316 (20)]	0.0228 (5) [0.024 (<10)]	0.3350 (4) [0.336 (20)]
Z	0.6885 (20) [0.677 (40)]	0.2063 (9) [0.204 (40)]	0.5522 (8) [0.552 (<10)]	0.1096 (9) [0.105 (10)]	0.9253 (8) [0.923 (20)]	0.5732 (9) [0.577 (10)]
β_{XX}	0.0122 (10)	0.0028 (3)	0.0063 (3)	0.0047 (4)	0.0029 (3)	0.0045 (3)
β_{YY}	0.0107 (12)	0.0042 (6)	0.0062 (5)	0.0045 (3)	0.0070 (5)	0.0042 (4)
β_{ZZ}	0.0259 (36)	0.0067 (13)	0.0082 (11)	0.0163 (14)	0.0127 (12)	0.0174 (15)
β_{XY}	−0.0021 (8)	0.0000 (4)	0.0009 (4)	0.0011 (3)	0.0012 (3)	−0.0008 (3)
β_{XZ}	0.0003 (15)	0.0003 (5)	−0.0010 (5)	0.0008 (6)	0.0015 (5)	−0.0016 (6)
β_{YZ}	−0.0075 (18)	−0.0016 (8)	−0.0011 (8)	−0.0025 (8)	0.0008 (8)	−0.0015 (8)

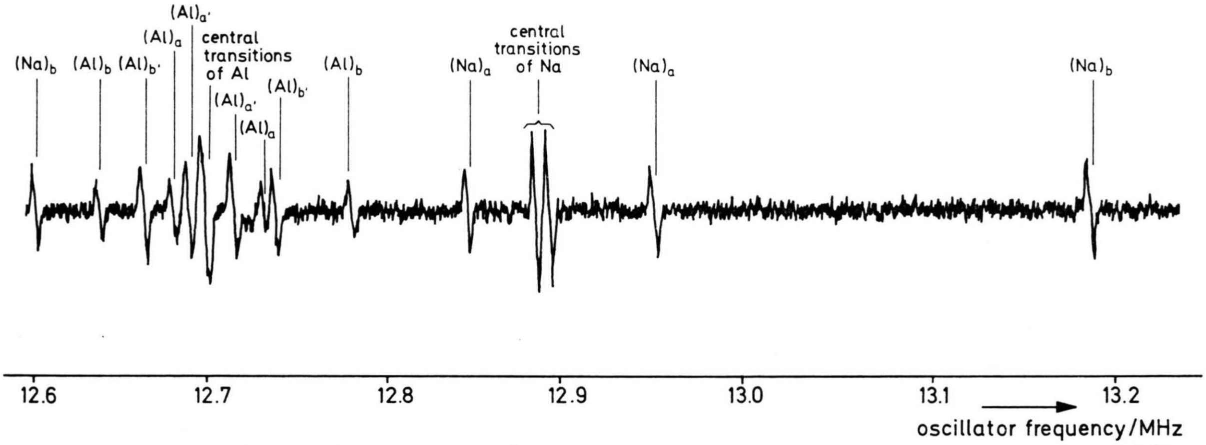

Fig. 2. NMR spectrum for a single crystal of $NaAlCl_4$ in a magnetic field $H_0 = 11.448$ kOe. The rotation axis $x' \perp \boldsymbol{H}_0$ is parallel to y'' (= [010]). A modulation amplitude of $\Delta H_{\text{mod}} \approx 2.34$ Oe ($\Delta \nu_{\text{mod}} \approx 2.6$ kHz, respectively) was used. The angle between $\boldsymbol{H}_0$ and z'' (= [001]) is 56.1°.

where

$$K = \frac{3\,e\,Q\,(2\,m-1)}{2\,I\,(2\,I-1)\,h} . \tag{5}$$

In Eqs. (1) – (5) the constants are defined as: e = charge of electron, Q = nuclear quadrupole moment, I = nuclear spin quantum number, m = magnetic quantum number of the spin, h = Planck's constant. The coefficients A_i, B_i, C_i, are not linearly independent. The following relations are valid [10]:

$$A_{x''} + A_{y''} + A_{z''} = 0 , \tag{6 a}$$

$$A_{x''} + B_{x''} = A_{z''} - B_{z''} , \tag{6 b}$$

$$A_{y''} + B_{y''} = A_{x''} - B_{x''} , \tag{6 c}$$

$$A_{z''} + B_{z''} = A_{y''} - B_{y''} . \tag{6 d}$$

Our coordinate system is chosen in such a way that one of the axes $x'' \parallel [100]$, $y'' \parallel [010]$, $z'' \parallel [001]$ is in turn the rotation axis x'. By cyclic permutation, using x'', y'', and z'' as the rotation axis x', the components of the electric field gradient tensor (EFG) with respect to the crystal axes are found.

Due to the small difference in the gyromagnetic ratio of ^{27}Al and of ^{23}Na, respectively, the NMR spectrum at ≈ 11.5 kOe is fairly crowded with lines in the frequency range 12.2 MHz $\lesssim \nu \lesssim$ 13.3 MHz. In Fig. 2 such a spectrum is shown as taken from the chart recorder.

The experimental results of ^{23}Na and ^{27}Al NMR in $NaAlCl_4$ are presented in Figs. 3, 4, and 5. The satellite frequency splittings $\Delta\nu_m$ $(m \neq 1/2)$ are shown as a function of the rotation angle α_i, which is defined in Figure 1. Whereas in Figs. 3 a and 3 b the crystal axis [100] served as the rotation axis perpendicular to $\boldsymbol{H}_0$, the results shown in Figs. 4 a and 4 b are gained by using the axis [010] as the rotation axis. In turn, Figs. 5 a and 5 b correspond to the axis [001] perpendicular to $\boldsymbol{H}_0$. From the satellite frequency splittings the coefficients A_i, B_i, and C_i $(i = x'', y'', z'')$ can be determined using the relations given in Equations (1) – (5). In Table 2 the coefficients as determined in this way are listed.

Table 2. Coefficients A_i, B_i, C_i $(i = x'', y'', z'')$ of the ^{23}Na and ^{27}Al NMR rotation spectra according to Equation (1).

	Rotation axis: [100]			Rotation axis: [010]			Rotation axis: [001]		
Nucleus	$A_{x''}$/MHz	$B_{x''}$/MHz	$C_{x''}$/MHz	$A_{y''}$/MHz	$B_{y''}$/MHz	$C_{y''}$/MHz	$A_{z''}$/MHz	$B_{z''}$/MHz	$C_{z''}$/MHz
Na_a	0.2999	0.0793	−0.7397	−0.1903	0.4105	0.2593	−0.1091	−0.4901	−0.2253
Na_b	0.3005	0.0796	0.7393	−0.1906	0.4109	−0.2585	−0.1101	−0.4898	0.2242
Al_a	−0.0661	0.3737	−0.1117	−0.1535	−0.2851	0.1025	0.2200	−0.0877	−0.6680
$Al_{a'}$	−0.0330	0.1868	−0.0558	−0.0770	−0.1425	0.0511	0.1100	−0.0435	−0.3340
Al_b	−0.0661	0.3741	0.1105	−0.1539	−0.2848	−0.1031	0.2193	−0.0881	0.6681
$Al_{b'}$	−0.0331	0.1868	0.0554	−0.0768	−0.1426	−0.0519	0.1100	−0.0445	0.3341

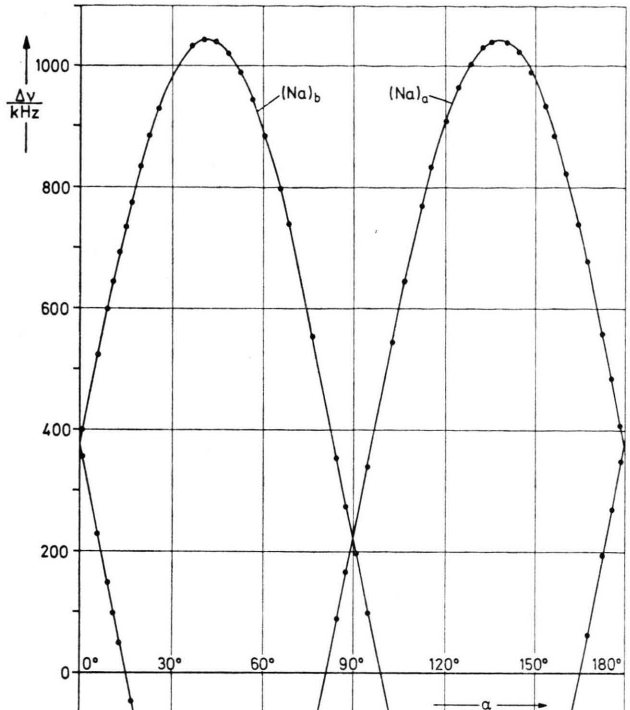

Fig. 3 a. NMR rotation diagram of ^{23}Na in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [100] $\perp \boldsymbol{H}_0$. An external field of ≈ 13.45 kOe was applied during these experiments. Plotted is $\Delta\nu(^{23}\text{Na}) = |\nu(1/2 \rightleftharpoons 3/2) - |\nu(-1/2 \rightleftharpoons -3/2)|$ as a function of the rotation angle α.

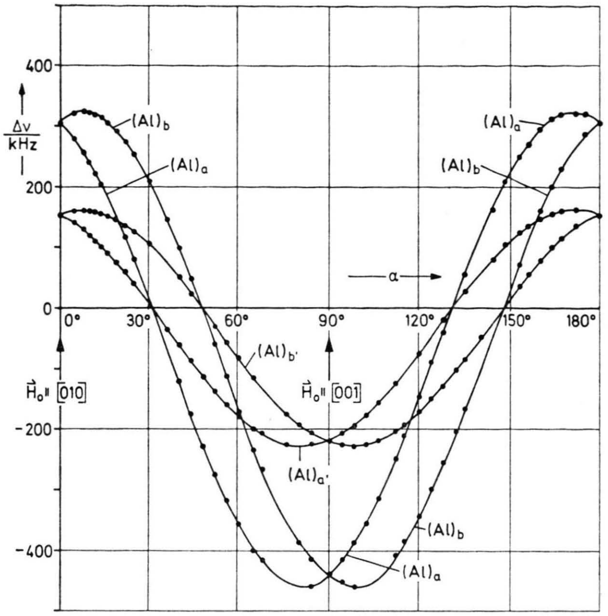

Fig. 3 b. NMR rotation diagram of ^{27}Al in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [100] $\perp$ $\boldsymbol{H}_0$. An external field of ≈ 13.45 kOe was applied during these experiments. Plotted is $\Delta\nu_{a'(b')}(^{27}\text{Al}) = |\nu(1/2 \rightleftharpoons 3/2)| - |\nu(-1/2 \rightleftharpoons -3/2)|$ and $\Delta\nu_{a(b)}(^{27}\text{Al}) = |\nu(3/2 \rightleftharpoons 5/2) - |\nu(-3/2 \rightleftharpoons -5/2)|$ as a function of the rotation angle α.

With the aid of these coefficients and with Eqs. (2), (3), and (4), the components $K \cdot V_{i''j''}$ of the nuclear quadrupole coupling tensors of ^{23}Na and ^{27}Al (in the frame of the crystal axes system x'', y'', z'') follow. Together with the appropriate combinations of signs they are given in Table 3.

Using an appropriate computer program the tensors $K \cdot V_{i''j''}$ were diagonalized, yielding the new tensors $K \cdot V_{ij}$ $(i, j = x, y, z)$ with $V_{ij} \neq 0$ for $i = j$, $V_{ij} = 0$ for $i \neq j$; $|V_{xx}| \leqq |V_{yy}| \leqq |V_{zz}|$; $V_{xx} + V_{yy} + V_{zz} = 0$.

In the following we shall use the abbreviation $V_{zz} \equiv e\,q$; asymmetry parameter

$$\eta = (V_{xx} - V_{yy})/V_{zz}\,, \quad 0 \leqq \eta \leqq 1\,;$$

nuclear quadrupole coupling constant $|e^2 q\,Q/h|$ (given in MHz). The results of the diagonalization are given in Table 4. In this table each of the two

$K \cdot V_{i''j''}$	Combination of signs a b c d	^{23}Na $K \cdot V_{i''j''}$ / MHz	Combination of signs a b c d	^{27}Al $K \cdot V_{i''j''}$ / MHz
$K \cdot V_{x''x''}$	− − − −	0.60040 ± 0.00038	+ + + +	0.13178 ± 0.00033
$K \cdot V_{y''y''}$	+ + + +	0.38030 ± 0.00032	+ + + +	0.30756 ± 0.00030
$K \cdot V_{z''z''}$	+ + + +	0.22007 ± 0.00040	− − − −	0.43942 ± 0.00023
$K \cdot V_{y''z''}$	+ + − −	0.73950 ± 0.00014	− − + +	0.11115 ± 0.00048
$K \cdot V_{z''x''}$	+ − + −	0.25890 ± 0.00028	− + − +	0.10290 ± 0.00067
$K \cdot V_{x''y''}$	+ − − +	0.22475 ± 0.00039	− + + −	0.66808 ± 0.00009

Table 3. Components of the nuclear quadrupole coupling tensors of ^{23}Na and ^{27}Al in NaAlCl$_4$ within the frame of the crystal axes system x'', y'', z''. The combinations of signs assigned to a, b, c, and d, correspond to the four crystallographically possible orientations of the nuclear quadrupole coupling tensor.

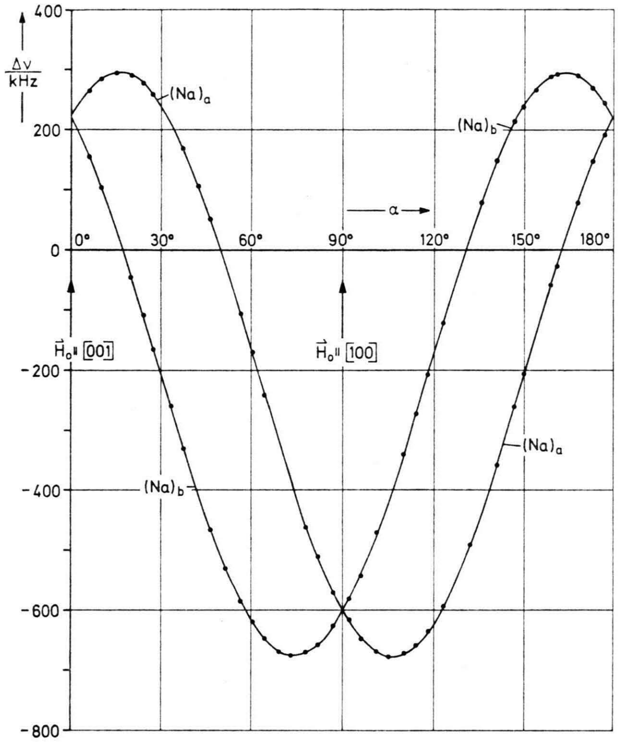

Fig. 4 a. NMR rotation diagram of ^{23}Na in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [010] ⊥ $\boldsymbol{H}_0$. An external field of ≈ 11.47 kOe was applied during these experiments. Plotted is $\Delta\nu\,(^{23}\mathrm{Na}) = |\,\nu\,(1/2 \rightleftharpoons 3/2) - |\,\nu\,(-1/2 \rightleftharpoons -3/2)\,|$ as a function of the rotation angle α.

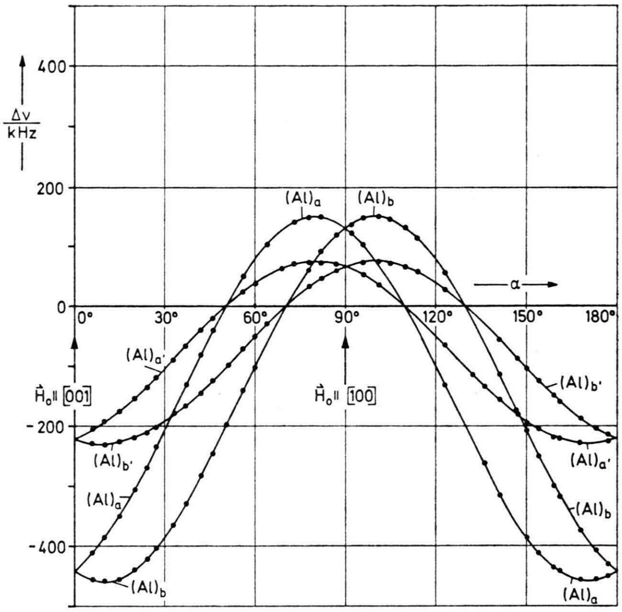

Fig. 4 b. NMR rotation diagram of ^{27}Al in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [010] ⊥ $\boldsymbol{H}_0$. An external field of ≈ 11.47 kOe was applied during these experiments. Plotted is $\Delta\nu_{\mathrm{a}'(\mathrm{b}')}\,(^{27}\mathrm{Al}) = |\,\nu\,(1/2 \rightleftharpoons 3/2)\,| - |\,\nu\,(-1/2 \rightleftharpoons -3/2)$ and $\Delta\nu_{\mathrm{a}(\mathrm{b})}\,(^{27}\mathrm{Al}) = |\,\nu\,(3/2 \rightleftharpoons 5/2)\,| - |\,\nu\,(-3/2 \rightleftharpoons -5/2)\,|$ as a function of the rotation angle α.

nuclear quadrupole coupling tensors V_{ij} (^{23}Na) and V_{ij} (^{27}Al), appear with four possible combinations of signs (a, b, c, d). These combinations correspond to the four crystallographically equivalent positions of Na and Al, in the space group P$2_1 2_1 2_1$. As in other investigations [11–13] of this kind, two tensors of different magnitude and orientation can be calculated from the frequency splittings for ^{23}Na as well as for ^{27}Al. We decided between the possible tensors by determining the maximum frequency splitting for ^{23}Na and ^{27}Al experimentally and by comparing experimental and calculated values of $\Delta\nu$.

The first order perturbation theory of Volkoff [10] as applied to the NMR investigation of ^{23}Na and ^{27}Al at ≈ 13.5 kOe is justified, as field dependent experiments have shown. The frequency splitting $\Delta\nu$ (^{23}Na) was investigated for different fields H_0 in the range 13.430 kOe $\geqq H_0 \geqq$ 3.004 kOe. In this

	^{23}Na a b c d		^{27}Al a b c d	
$\left\|\frac{e^2 q Q}{h}\right\| \cdot \frac{1}{\mathrm{MHz}}$		1.1117 ± 0.0006		1.4895 ± 0.0012
η		0.2153 ± 0.0005		0.3375 ± 0.0011
$R_{x,[100]}$	+ + − −	0.1728 ± 0.0012	− − + +	0.5249 ± 0.0006
$R_{x,[010]}$	− + − +	0.6869 ± 0.0012	− + − +	0.4477 ± 0.0006
$R_{x,[001]}$	+ − − +	0.7059 ± 0.0012	+ − − +	0.7239 ± 0.0006
$R_{y,[100]}$	+ + − −	0.9655 ± 0.0012	+ + − −	0.5395 ± 0.0006
$R_{y,[010]}$	− + − +	0.0238 ± 0.0012	+ − + −	0.4828 ± 0.0006
$R_{y,[001]}$	− + + −	0.2595 ± 0.0012	+ − − +	0.6898 ± 0.0006
$R_{z,[100]}$	+ + − −	0.1950 ± 0.0012	− − + +	0.6583 ± 0.0006
$R_{z,[010]}$	+ − + −	0.7264 ± 0.0012	+ − + −	0.7526 ± 0.0006
$R_{z,[001]}$	+ − − +	0.6591 ± 0.0012	− + + −	0.0119 ± 0.0006

Table 4. Quadrupole coupling constant, $|\,e^2 q\,Q/h\,|$, asymmetry parameter η, and direction cosines for ^{23}Na and ^{27}Al in NaAlCl$_4$ at room temperature. R_{ij} $\{i = x,\ y,\ z;\ j = x''\ (= [100]),\ y''\,(= [010]),\ z''\,(= [001])\}$ is the direction cosine of the angle between the i-axis of the nuclear quadruple coupling tensor and the j-axis of the crystal. The combinations of signs assigned to a, b, c, and d, correspond to the four crystallographically possible orientations of the nuclear quadrupole coupling tensor. Errors given are maximum mean errors.

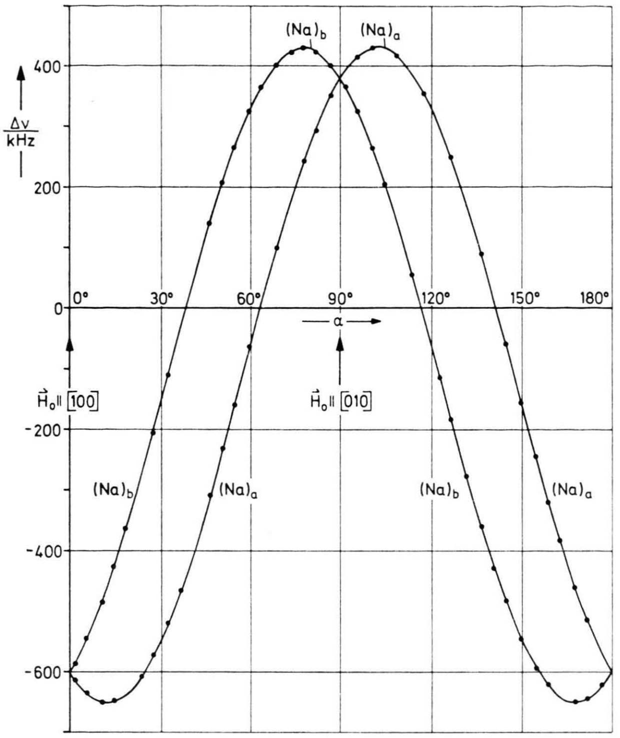

Fig. 5 a. NMR rotation diagram of ^{23}Na in $NaAlCl_4$ at room temperature. Rotation axis is the crystal axis $[001] \perp \boldsymbol{H}_0$. An external field of ≈ 11.47 kOe was applied during these experiments. Plotted is $\Delta\nu(^{23}Na) = |\nu(1/2 \rightleftharpoons 3/2)| - |\nu(-1/2 \rightleftharpoons -3/2)|$ as a function of the rotation angle α.

range the splitting of 675.5 kHz found for a particular orientation of the crystal at $H_0 = 13.430$ kOe did not change more than ± 1 kHz by varying H_0 within the limits given above, a shift which is within the limits of error. Therefore, the theoretical approximation used is appropriate for ^{23}Na as well as for ^{27}Al in $NaAlCl_4$.

3. *NQR of ^{35}Cl in $NaAlCl_4$*

Of the two isotopes ^{35}Cl and ^{37}Cl mainly the NQR signals of ^{35}Cl were studied. Since the four Cl atoms of the "ion" $[AlCl_4]^{\ominus}$ are crystallographically inequivalent (see crystal structure data of Table 1), four ^{35}Cl NQR lines are expected from measurements at room temperature and without ap-

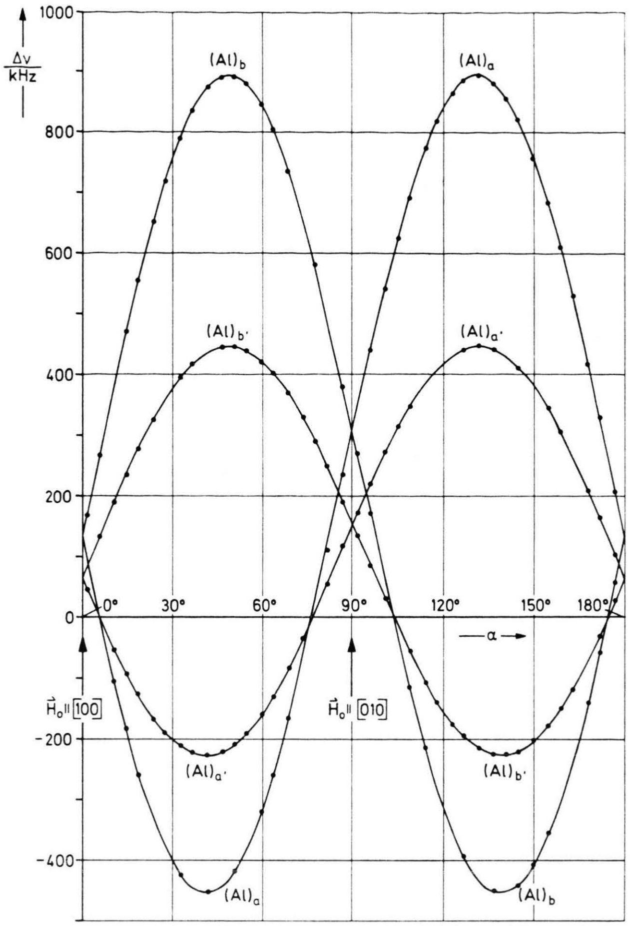

Fig. 5 b. NMR rotation diagram of ^{27}Al in $NaAlCl_4$ at room temperature. Rotation axis is the crystal axis $[001] \perp \boldsymbol{H}_0$. An external field of ≈ 11.47 kOe was applied during these experiments. Plotted is $\Delta\nu_{a'(b')}(^{27}Al) = |\nu(1/2 \rightleftharpoons 3/2)| - |\nu(-1/2 \rightleftharpoons -3/2)$ and $\Delta\nu_{a(b)}(^{27}Al) = |\nu(3/2 \rightleftharpoons 5/2)| - |\nu(-3/2 \rightleftharpoons -5/2)|$ as a function of the rotation angle α.

Table 5. Pure NQR frequencies ν of $^{35}Cl_{A...D}$ and $^{37}Cl_{A...D}$ at room temperature; frequency ratios $\nu(^{35}Cl)/\nu(^{37}Cl)$ of $Cl_{A...D}$.

Nucleus	$\frac{\nu}{MHz}$ $(T = 295 \pm 1\ K)$ [a]	$\frac{\nu}{MHz}$ $(T = 297 \pm 1\ K)$ [b]	Nucleus	$\frac{\nu}{MHz}$ $(T = 295 \pm 1\ K)$ [a]	$\nu(^{35}Cl)/\nu(^{37}Cl)$ [c]
$^{35}Cl_A$	11.0100 ± 0.0005	11.009	$^{37}Cl_A$	8.6772 ± 0.0015	1.26884 ± 0.00028
$^{35}Cl_B$	11.2772 ± 0.0005	11.272	$^{37}Cl_B$	8.8879 ± 0.0015	1.26883 ± 0.00027
$^{35}Cl_C$	11.3959 ± 0.0005	11.385	$^{37}Cl_C$	8.9818 ± 0.0015	1.26878 ± 0.00027
$^{35}Cl_D$	11.5799 ± 0.0005	11.583	$^{37}Cl_D$	9.1250 ± 0.0015	1.26903 ± 0.00027

[a] This paper. [b] Evans and Lo [14].
[c] $\langle \nu(^{35}Cl)/\nu(^{37}Cl) \rangle = 1.26887 \pm 0.00028$; literature values [16]: $\nu(^{35}Cl)/\nu(^{37}Cl) = 1.26858 \pm 0.00040$.

Table 6. Pure NQR frequencies ν as function of the temperature; mean absolute and relative temperature coefficients of NQR frequency $\Delta\nu/\Delta T$ and $\frac{1}{\nu}\cdot\frac{\Delta\nu}{\Delta T}$ of $^{35}Cl_{A\ldots D}$.

	ν/MHz					
	T/K					
Nucleus	77.4 ± 1.0	275 ± 2	295 ± 1	305 ± 1	$\frac{\Delta\nu}{\Delta T}\frac{K}{kHz}$	$10^4\cdot\frac{1}{\nu}\frac{\Delta\nu}{\Delta T}K$
$^{35}Cl_A = ^{35}Cl_{III}$	11.282 ± 0.003	11.043 ± 0.003	11.0100 ± 0.0005	10.998 ± 0.003	−1.25	−1.12
$^{35}Cl_B = ^{35}Cl_{IV}$	11.459 ± 0.003	11.302 ± 0.003	11.2772 ± 0.0005	11.267 ± 0.003	−0.84	−0.74
$^{35}Cl_C = ^{35}Cl_{II}$	11.605 ± 0.003	11.421 ± 0.003	11.3959 ± 0.0005	11.385 ± 0.003	−0.88	−0.76
$^{35}Cl_D = ^{35}Cl_I$	11.861 ± 0.003	11.613 ± 0.003	11.5799 ± 0.0005	11.563 ± 0.003	−1.31	−1.12

plication of an external magnetic field $\boldsymbol{H}_0$. Evans and Lo [14] have investigated the ^{35}Cl NQR spectrum of polycrystalline samples of $NaAlCl_4$ at room temperature ($\approx 24\ ^\circ C$) and their data are in good agreement with the data we found at $T = 295\ K \pm 1\ K$ ($22\ ^\circ C \pm 1\ ^\circ C$). The room temperature data were also confirmed recently by Merryman et alii [15]. In Table 5 our experimental results are given together with the ^{37}Cl NQR frequencies. These data were measured using single crystals of $NaAlCl_4$ and a crossed coil spectrometer.

The ^{35}Cl resonance frequencies were studied as a function of the temperature with a superregenerative NQR spectrometer. The results are shown in Table 6 and a plot $\nu = f(T)$ is shown in Figure 6. The mean slope of the curves $\nu = f(T)$ is given too, together with the mean temperature coefficient $1/\nu \cdot \Delta\nu/\Delta T$ for the temperature range $77.4\ K \leqq T \leqq 305\ K$. From the data of Table 6 and from Fig. 6 it follows that according to the temperature behaviour of the NQR frequencies there are two groups of Cl atoms distinguishable. Whereas $\langle 1/\nu \cdot \Delta\nu/\Delta T \rangle = -0.935 \cdot 10^{-4}\ K^{-1}$ for $^{35}Cl_{A\ldots D}$, $1/\nu \cdot \Delta\nu/\Delta T$ for Cl_A and for Cl_D is about 50% higher than $1/\nu \cdot \Delta\nu/\Delta T$ for Cl_B and Cl_C, respectively.

Zeeman spectra were studied to determine the nuclear quadrupole coupling constant of ^{35}Cl in $NaAlCl_4$, the orientation of the nuclear quadrupole coupling tensor of ^{35}Cl, and the asymmetry parameter η. The NQR frequency ν_Q for the transition $m = \pm 1/2 \rightleftharpoons m' = \pm 3/2$ for a nucleus with $I = 3/2$ is connected with the nuclear quadrupole coupling constant and the asymmetry parameter η by

$$\nu_Q = \frac{e^2 q Q}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \equiv \frac{e^2 q Q}{2h}\varrho . \qquad (7)$$

First order Zeeman splitting of ν_Q by weak magnetic fields gives four lines which in the frequency scale are symmetric about the locus of ν_Q. The frequencies of the four lines are given by [17]:

$$\nu = \nu_Q \pm \frac{\nu_L}{2}([m_1] \pm [m_2]) , \qquad (8)$$
$$(m_1 = 1/2;\ m_2 = 3/2) .$$

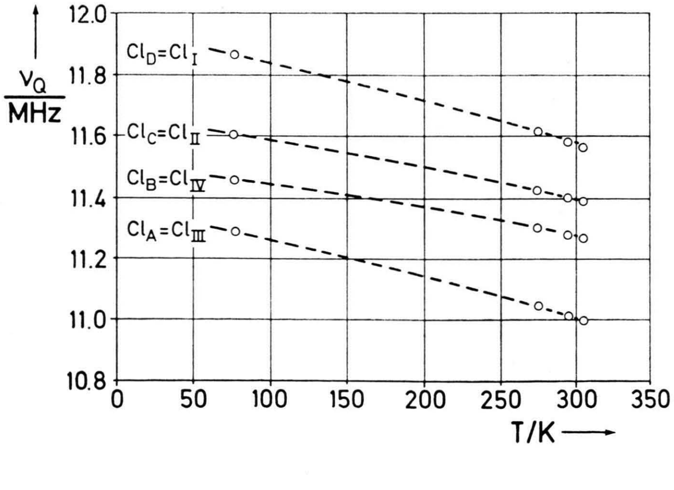

Fig. 6. Temperature dependence of ^{35}Cl NQR frequencies as a function of the temperature in the range $77.4\ K \leqq T \leqq 305\ K$.

ν_L is the Larmor frequency of the nucleus ($I = 3/2$) considered, and

$$[m_i] = [a^2_{m_i} \cos^2 \Theta + (b^2_{m_i} + c^2_{m_i} + 2\, b_{m_i} c_{m_i} \cos 2\, \Phi) \sin^2 \Theta]^{1/2} . \tag{8 a}$$

Θ is the polar angle between the z-direction of the EFG tensor and the direction z' of the magnetic field $\boldsymbol{H}_0$. φ is the azimuthal angle between the x-direction of the EFG tensor and the projection of the magnetic field vector $\boldsymbol{H}_0$ on the $(x y)$ plane of the EFG tensor (see Figure 7). The coefficients a_{m_i}, b_{m_i}, and c_{m_i}, respectively, are given by:

$$a_{1/2} = -1 + 2/\varrho ; \quad b_{1/2} = 1 + 1/\varrho ; \quad c_{1/2} = -\eta/\varrho ;$$
$$a_{3/2} = -1 - 2/\varrho ; \quad b_{3/2} = 1 - 1/\varrho ; \quad c_{3/2} = \eta/\varrho . \tag{8 b}$$

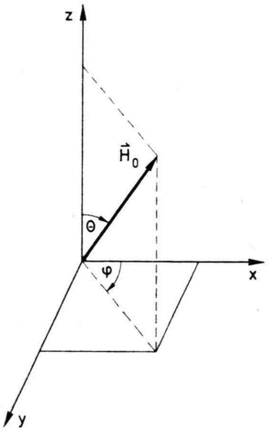

Fig. 7. Vector of the magnetic field $\boldsymbol{H}_0$ with respect to the coordinate system of the EFG tensor, x, y, z. Θ is the polar angle between z and the direction of $\boldsymbol{H}_0$. φ is the azimuthal angle between x and the projection of $\boldsymbol{H}_0$ on the $(x y)$-plane of the EFG tensor.

In the experiments reported here the line splitting of the inner pair of lines (α-pair)

$$\Delta\nu = \nu_L\,([m_1] - [m_2]) \tag{8 c}$$

was measured as a function of the rotation angle for the four crystallographically inequivalent Cl atoms at room temperature. To study the Zeeman spectra (α-pairs) of Cl$_A$, Cl$_B$, and Cl$_C$, the single crystals were rotated about the crystal axis [001], whereas for the study of $\Delta\nu$ (Cl$_D$), [100] was the rotation axis chosen. The results are shown in Figs. 8 through 11. Using a least squares program from the Zeeman splitting of the ^{35}Cl NQR spectra the data of the nuclear quadrupole coupling tensors of ^{35}Cl in NaAlCl$_4$ are found (see Table 7).

The assignment of the NQR data for Cl$_{A...D}$ to the chlorine positions Cl$_{I...IV}$ was done in Table 7 under certain assumptions about the chemical bond Cl – Al (see Discussion). The errors given in Table 7 for the nuclear quadrupole coupling constants of ^{35}Cl in NaAlCl$_4$ have been calculated by the usual least squares method. However, we wish to point out that for the data given in this Table, for Cl$_D \equiv$ Cl$_I$ the true error may be higher by almost a factor of 4. This is due to the accidental coincidence of the two phase shifted Zee-

Table 7. Quadrupole coupling constant, $|e^2 q Q/h|$, asymmetry parameter η, and direction cosines for ^{35}Cl$_{A...D}$ in NaAlCl$_4$ at room temperature. R_{ij} $\{i = x, y, z;\ i = x''\ (=[100]),\ y''(=[010]),\ z''(=[001])\}$ is the direction cosine of the angle between the i-axis of the nuclear quadrupole coupling tensor and the j-axis of the crystal. The combination of signs assigned to a, b, c, and d, correspond to the four crystallographically possible orientations of the nuclear quadrupole coupling tensor. Application of the operation $2_1 \parallel$ ([100], [010], [001]) to orientation a yields orientation b, c, and d, respectively. The errors given for the direction cosines are mean values.

	^{35}Cl$_A \equiv {}^{35}$Cl$_{III}$		^{35}Cl$_B \equiv {}^{35}$Cl$_{IV}$		^{35}Cl$_C \equiv {}^{35}$Cl$_{II}$		^{35}Cl$_D \equiv {}^{35}$Cl$_I$	
$\left\lvert \frac{e^2 q Q}{h} \right\rvert \cdot \frac{1}{\text{MHz}}$	21.646 ± 0.003		22.410 ± 0.016		22.520 ± 0.010		23.033 ± 0.030	
η	0.315 ± 0.007		0.197 ± 0.010		0.270 ± 0.005		0.182 ± 0.025	
	a b c d		a b c d		a b c d		a b c d	
$R_{x,[100]}$	+ + – –	0.191 ± 0.006	+ + – –	0.754 ± 0.019	+ + – –	0.203 ± 0.015	– – + +	0.002 ± 0.075
$R_{x,[010]}$	+ – + –	0.832 ± 0.006	+ – + –	0.116 ± 0.120	+ – + –	0.286 ± 0.015	+ – + –	1.000 ± 0.003
$R_{x,[001]}$	+ – – +	0.521 ± 0.007	+ – – +	0.647 ± 0.011	+ – – +	0.937 ± 0.003	– + + –	0.002 ± 0.013
$R_{y,[100]}$	– – + +	0.332 ± 0.008	– – + +	0.480 ± 0.018	– – + +	0.836 ± 0.008	+ + – –	0.998 ± 0.002
$R_{y,[010]}$	+ – + –	0.554 ± 0.009	+ – + –	0.575 ± 0.028	+ – + –	0.549 ± 0.014	+ – + –	0.000 ± 0.093
$R_{y,[001]}$	– + + –	0.764 ± 0.003	+ – – +	0.663 ± 0.010	+ – – +	0.014 ± 0.025	– + + –	0.062 ± 0.070
$R_{z,[100]}$	+ + – –	0.924 ± 0.002	+ + – –	0.448 ± 0.012	+ + – –	0.510 ± 0.004	– – + +	0.062 ± 0.070
$R_{z,[010]}$	+ – + –	0.03 ± 0.05	+ – + –	0.810 ± 0.008	+ – + –	0.786 ± 0.005	+ – + –	0.000 ± 0.093
$R_{z,[001]}$	– + + –	0.382 ± 0.003	– + + –	0.378 ± 0.003	– + + –	0.350 ± 0.005	+ – – +	0.998 ± 0.002

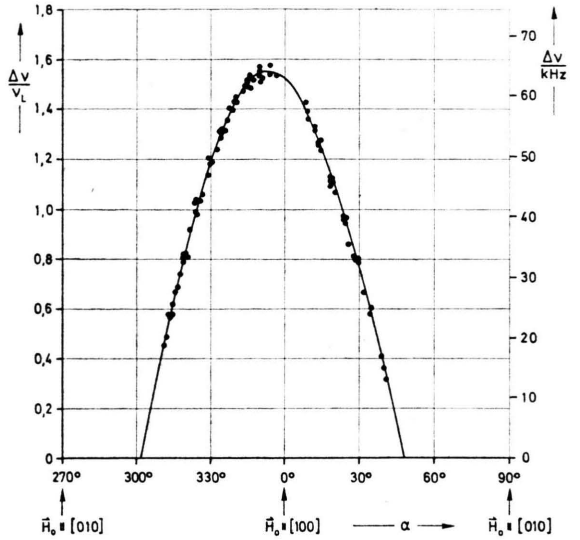

Fig. 8. NQR Zeeman rotation diagram of $^{35}\mathrm{Cl_A}$ in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [001] $\perp \boldsymbol{H}_0$. An external field of (98.7 ± 0.3) Oe was applied during these experiments. Plotted is $\Delta\nu(^{35}\mathrm{Cl_A}) = |\nu(-1/2 \rightleftharpoons -3/2)| - |\nu(1/2 \rightleftharpoons 3/2)|$ as a function of the rotation angle α.

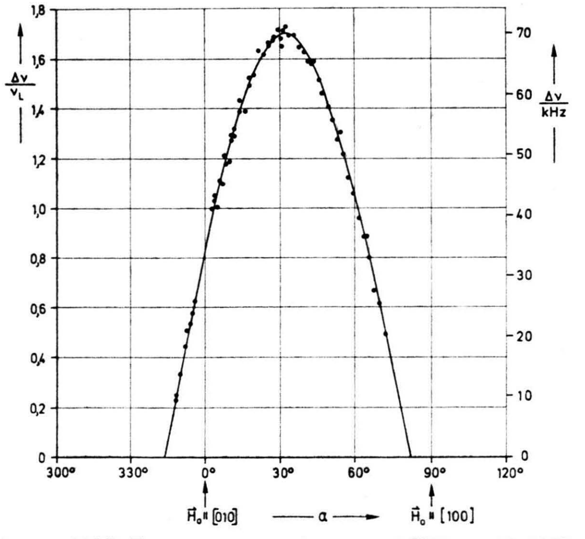

Fig. 9. NQR Zeeman rotation diagram of $^{35}\mathrm{Cl_B}$ in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [001] $\perp \boldsymbol{H}_0$. An external field of (98.7 ± 0.3) Oe was applied during these experiments. Plotted is $\Delta\nu(^{35}\mathrm{Cl_B}) = |\nu(-1/2 \rightleftharpoons -3/2)| - |\nu(1/2 \rightleftharpoons 3/2)|$ as a function of the rotation angle α.

man spectra of Cl$_\mathrm{D}$, which differ by an amount less than the line width and therefore cannot be separated.

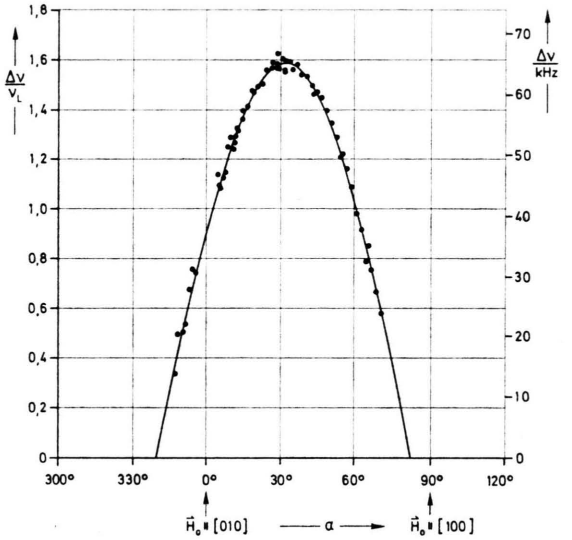

Fig. 10. NQR Zeeman rotation diagram of $^{35}\mathrm{Cl_C}$ in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [001] $\perp \boldsymbol{H}_0$. An external field of (98.7 ± 0.3) Oe was applied during these experiments. Plotted is $\Delta\nu(^{35}\mathrm{Cl_C}) = |\nu(-1/2 \rightleftharpoons -3/2)| - |\nu(1/2 \rightleftharpoons 3/2)|$ as a function of the rotation angle α.

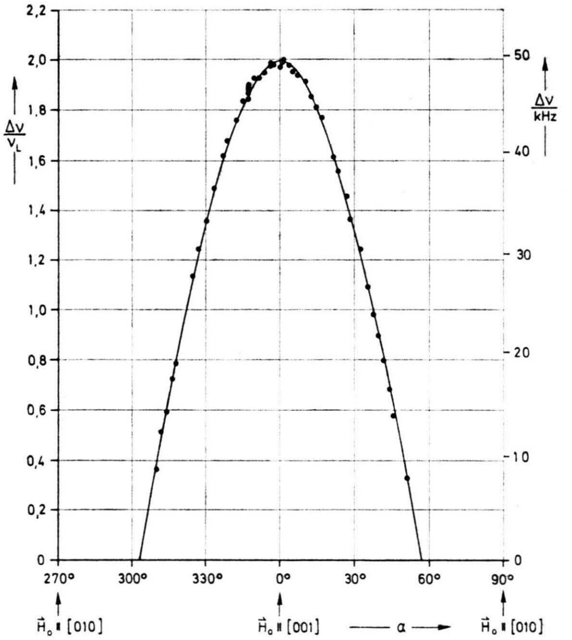

Fig. 11. NQR Zeeman rotation diagram of $^{35}\mathrm{Cl_D}$ in NaAlCl$_4$ at room temperature. Rotation axis is the crystal axis [100] $\perp \boldsymbol{H}_0$. An external field of (59.1 ± 0.2) Oe was applied during these experiments. Plotted is $\Delta\nu(^{35}\mathrm{Cl_D}) = |\nu(-1/2 \rightleftharpoons -3/2)| - |\nu(1/2 \rightleftharpoons 3/2)|$ as a function of the rotation angle α.

IV. Discussion

The discussion of the NQR data of $\mathrm{NaAlCl_4}$ with respect to the crystal structure is restricted here to the situation at room temperature. This restriction is however not severe, since from our NQR data we find no phase transition in the range $77.4\,\mathrm{K} \leqq T \leqq 305\,\mathrm{K}$. For quite a number of compounds, i. e. $\mathrm{Me^IMe^{III}X_4}$, $\mathrm{Me^I}$ = alkali-metal ion, $\mathrm{Me^{III}}$ = B, Al, Ga, In, and X = F, Cl, Br, I, phase transformations have been observed. Examples for the detection of phase transformations by NQR are the compounds $\mathrm{Me^IAlBr_4}$ ($\mathrm{Me^I} = \mathrm{Na}$)[18], and $\mathrm{Me^IGaCl_4}$ ($\mathrm{Me^I} = \mathrm{Ga^I}$, K)[19]. ^{35}Cl and ^{69}Ga NQR data on polycrystalline material of compounds containing the ion $\mathrm{AlCl_4}^{\ominus}$ have recently been discussed by Merryman et al.[15, 20] and for compounds containing the ions $\mathrm{GaCl_4}^{\ominus}$ and $\mathrm{Ga_2Cl_7}^{\ominus}$, respectively, by Deeg and Weiss[19] (cf. ref. cited in [15, 19, 20]). From single crystal data more detailed information is expected.

The $\overline{\mathrm{Al}-\mathrm{Cl}}$ distances within a tetrahedron $\mathrm{AlCl_4}^{\ominus}$ are between 2.11 and 2.16 Å according to the crystal structure determination of Baenziger[2]. From our refinement a somewhat smaller spread of distances results ($2.121\,\text{Å} \leqq d(\overline{\mathrm{Al}-\mathrm{Cl}}) \leqq 2.144\,\text{Å}$), see Table 8. An analysis of the data of Table 8 shows that the mean distance $\langle d(\overline{\mathrm{Al}-\mathrm{Cl}}) \rangle$ within a tetrahedron $\mathrm{AlCl_4}^{\ominus}$ is $2.134\,\text{Å} \pm 0.013\,\text{Å}$. The spread of the values $d(\overline{\mathrm{Al}-\mathrm{Cl}})$ is within the limit of error (± 0.025 Å), whereas the deviations of the $\overline{\mathrm{Cl}-\mathrm{Cl}}$ distances within the tetrahedron $[\langle d(\overline{\mathrm{Cl}-\mathrm{Cl}}) \rangle = 3.483 \pm 0.080\,\text{Å}]$ are larger than the limit of error (± 0.025 Å). The main distortion of the tetrahedron $\mathrm{AlCl_4}^{\ominus}$ is therefore an angular one. Particularly the angle ($\mathrm{Cl_{III}}-\mathrm{Al}-\mathrm{Cl_{IV}}$) is smaller than the regular tetrahedron angle of $109' 28''$ by about 4 degrees, whereas the error in the determination of the angles via the atomic coordinates and the lattice constants is ± 0.5 degrees.

No qualitative relation between $|e^2 q Q/h|$ (^{35}Cl) and the bond length $d(\overline{\mathrm{Al}-\mathrm{Cl}})$ can be given from the results of our experiments. The spread of the coupling constants is small as is the spread in bond length $d(\overline{\mathrm{Al}-\mathrm{Cl}})$. A similar conclusion was drawn by Merryman et al.[15] when comparing NQR

Atom A	Coordinates (X Y Z)	Atom B	Coordinates (X Y Z)	Distance d(A−B) Å
Al	(0.0380, 0.4857, 0.2063)	$\mathrm{Cl_I}$	(0.0320, 0.4919, 0.5552)	2.143 ± 0.025
Al	(0.0380, 0.4857, 0.2063)	$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 0.1096)	2.121 ± 0.025
Al	(0.0380, 0.4857, 0.2063)	$\mathrm{Cl_{III}}$	(−0.1531, 0.4772, 0.0747)	2.137 ± 0.025
Al	(0.0380, 0.4857, 0.2063)	$\mathrm{Cl_{IV}}$	(0.1227, 0.6650, 0.0732)	2.144 ± 0.025
$\mathrm{Cl_I}$	(0.0320, 0.4919, 0.5522)	$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 0.1096)	3.464 ± 0.025
$\mathrm{Cl_I}$	(0.0320, 0.4919, 0.5522)	$\mathrm{Cl_{III}}$	(−0.1531, 0.4772, 0.0747)	3.523 ± 0.025
$\mathrm{Cl_I}$	(0.0320, 0.4919, 0.5522)	$\mathrm{Cl_{IV}}$	(0.1227, 0.6650, 0.0732)	3.551 ± 0.025
$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 0.1096)	$\mathrm{Cl_{III}}$	(−0.1531, 0.4772, 0.0747)	3.507 ± 0.025
$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 0.1096)	$\mathrm{Cl_{IV}}$	(0.1227, 0.6650, 0.0732)	3.481 ± 0.025
$\mathrm{Cl_{III}}$	(−0.1531, 0.4772, 0.0747)	$\mathrm{Cl_{IV}}$	(0.1227, 0.6650, 0.0732)	3.403 ± 0.025
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 1.1096)	2.811 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{III}}$	(0.1531, −0.0228, 0.4253)	2.851 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{IV}}$	(0.3773, 0.3350, 0.5732)	2.965 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_I}$	(0.0320, 0.4919, 0.5522)	3.057 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{IV}}$	(−0.1227, 0.1650, 0.4268)	3.064 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_I}$	(−0.0320, −0.0081, 0.9478)	3.154 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{III}}$	(0.3469, 0.0228, 0.9253)	3.301 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	$\mathrm{Cl_{II}}$	(0.1481, 0.3153, 0.1096)	3.735 ± 0.035
Na	(0.1251, 0.2116, 0.6885)	Al	(−0.0380, −0.0143, 0.2937)	3.717 ± 0.035

Configuration ($\mathrm{Cl}_i-\mathrm{Al}-\mathrm{Cl}_j$)	Angle/Degree
($\mathrm{Cl_I}-\mathrm{Al}-\mathrm{Cl_{II}}$)	108.67 ± 0.5
($\mathrm{Cl_I}-\mathrm{Al}-\mathrm{Cl_{III}}$)	110.80 ± 0.5
($\mathrm{Cl_I}-\mathrm{Al}-\mathrm{Cl_{IV}}$)	111.83 ± 0.5
($\mathrm{Cl_{II}}-\mathrm{Al}-\mathrm{Cl_{III}}$)	110.88 ± 0.5
($\mathrm{Cl_{II}}-\mathrm{Al}-\mathrm{Cl_{IV}}$)	109.38 ± 0.5
($\mathrm{Cl_{III}}-\mathrm{Al}-\mathrm{Cl_{IV}}$)	105.26 ± 0.5

Table 8. Interatomic distances and angles in solid $\mathrm{NaAlCl_4}$; the error of $\pm 0.025\,(0.035)$ Å respectively ± 0.5 degrees is the maximum error resulting from the limits of error of the position parameters.

frequencies of tetrachloroaluminates and the bond length d(Al – Cl) in these solids.

The first coordination sphere of the ion $Na^{\oplus}$ in $NaAlCl_4$ is built up by 7 ions which are within $2.811\ \text{Å} \leqq d(\overline{Na-Cl}) \leqq 3.301\ \text{Å}$; the next Cl neighbor (the 8th) is then already 3.74 Å distant from the ion $Na^{\oplus}$. It is probably safe to consider the bond of the sodium to its neighbors in $NaAlCl_4$ as a purely ionic one, since the smallest distance $d(\overline{Na-Cl})$ in $NaAlCl_4$ is comparable with $d(\overline{Na^{\oplus}-Cl^{\ominus}})$ in NaCl ($d = 2.820$ Å at room temperature). The nuclear quadrupole coupling constant of ^{23}Na in $NaAlCl_4$ is typical for an ionic compound. This can be seen from data found for other ionic compounds as shown in Table 9.

From the single crystal measurements reported here, the additional information is a set of direction cosines of the EFG tensor and the asymmetry parameter η for each of the atoms in the unit cell.

Table 9. Nuclear quadrupole coupling constants $|e^2 q Q/h|$ and asymmetry parameters η of ^{23}Na in some inorganic compounds.

Compound	$\lvert e^2 q Q/h \rvert$ kHz	η	T/°C	Reference
$NaNO_3$	334	0	23	21
$NaNO_2$	1099.8	0.110	18	22
$NaIO_4$	49.0	0	23	23
$NaBF_4$	1008.4	0.095	23	1
$NaAlCl_4$	1111.7	0.215	~23	This paper
$NaXO_2$ [a]	538...3295	0	23	24
Na_2SO_4 (Thenardite)	2590	0.605	~23	25
$NaAl(SO_4)_2 \cdot 12\,H_2O$	163.2	0	17.3	26
$Na_2ZnCl_4 \cdot 3\,H_2O$	261.7	0	22.5	27

[a] X = Tl, Al, Se, In, Cr, Ti.

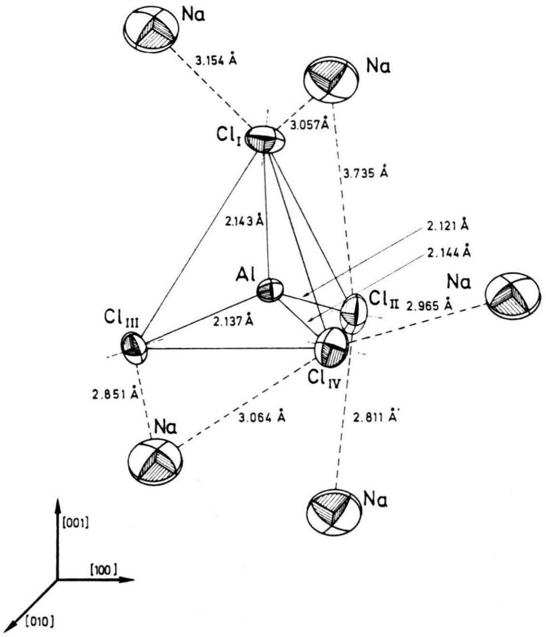

Fig. 12. Representation of the $AlCl_4^{\ominus}$-tetrahedron and its first coordination sphere.

Angle / Degree	a	b	c	d	Δ (Angle / Degree)
			$Al-Cl_I$		
α	93.6 (91.7)	93.6 (91.7)	86.4 (88.3)	86.4 (88.3)	±5 (±1)
β	90.0 (88.4)	90.0 (91.6)	90.0 (88.4)	90.0 (91.6)	±5 (±1)
γ	3.6 (2.6)	176.4 (177.4)	176.4 (177.4)	3.6 (2.6)	±10 (±5)
			$Al-Cl_{II}$		
	a	b	c	d	
α	59.3 (57.6)	59.3 (57.6)	120.7 (122.4)	120.7 (122.4)	±1 (±1)
β	38.2 (37.3)	141.8 (142.7)	38.2 (37.3)	141.8 (142.7)	±1 (±1)
γ	110.5 (106.4)	69.5 (73.6)	69.5 (73.6)	110.5 (106.4)	±1 (±1)
			$Al-Cl_{III}$		
	a	b	c	d	
α	22.5 (22.5)	22.5 (22.5)	157.5 (157.5)	157.5 (157.5)	±1 (±2)
β	88.3 (87.7)	91.7 (92.3)	88.3 (87.7)	91.7 (92.3)	±3 (±1)
γ	112.5 (112.4)	67.5 (67.6)	67.5 (67.6)	112.5 (112.4)	±1 (±1)
			$Al-Cl_{IV}$		
	a	b	c	d	
α	63.4 (65.9)	63.4 (65.9)	116.6 (114.1)	116.6 (114.1)	±1 (±1)
β	35.9 (34.1)	144.1 (145.9)	35.9 (34.1)	144.1 (145.9)	±1 (±1.5)
γ	112.2 (112.6)	67.8 (67.4)	67.8 (67.4)	112.2 (112.6)	±1 (±1)

Table 10. Angles α, β, γ, between the crystal axes [100], [010], and [001], respectively, and the z axes of the corresponding Cl_i EFG tensors (i = I, ..., IV). In brackets the angles α, β and γ between [100], [010] and [001], respectively, and the directions of the $Al-Cl_i$ bonds are given. a, b, c and d correspond to the different combinations of signs of the direction cosines, see legend to Table 4. Δ is the mean error of the corresponding angle.

Table A. Experimental (Y_{obs}) and calculated (Y_{calc}) structure amplitudes of NaAlCl$_4$. Absolute values are given.

h	k	l	$\lvert Y_{\mathrm{obs}} \rvert$	$\lvert Y_{\mathrm{calc}} \rvert$
0	2	0	52.7965	53.8661
0	4	0	98.6296	99.5800
0	6	0	124.4130	125.5519
0	10	0	27.7939	28.6285
0	1	1	15.6357	11.7386
0	2	1	35.9650	30.9423
0	4	1	11.3097	13.4883
0	5	1	26.6557	26.1617
0	6	1	50.0847	49.4164
0	7	1	10.5796	13.9986
0	10	1	17.5175	15.9086
0	11	1	19.7415	20.9336
0	0	2	69.0656	59.5403
0	1	2	113.0424	125.2969
0	2	2	35.8278	34.1777
0	5	2	76.5168	77.9056
0	6	2	35.0046	33.5016
0	7	2	44.9778	45.3693
0	9	2	12.4089	10.6482
0	10	2	8.5199	5.6778
0	2	3	15.3393	10.5283
0	3	3	17.4244	14.5932
0	5	3	13.0560	8.4571
0	7	3	23.4479	20.4705
0	8	3	13.3270	11.6173
0	0	4	23.4391	20.7677
0	1	4	50.7148	55.2597
0	2	4	29.7029	32.8605
0	4	4	13.4490	10.9179
0	5	4	45.4521	46.4604
0	6	4	9.9495	8.1656
0	7	4	15.2258	16.1917
0	8	4	23.2460	22.4375
0	9	4	9.4448	8.2630
0	4	5	21.2592	24.5008
0	0	6	38.0890	43.8345
0	1	6	36.9338	40.4960
0	2	6	10.8405	15.0832
0	3	6	48.8126	50.1606
0	4	6	8.7198	6.2328
0	5	6	18.6033	18.9064
0	6	6	30.1788	33.1212
0	1	7	8.9044	10.4083
1	1	0	8.9690	6.9687
1	3	0	71.9220	81.5855
1	4	0	48.8913	49.9669
1	5	0	18.8342	14.3086
1	6	0	35.5554	35.4504
1	7	0	12.9689	13.9340
1	8	0	23.1933	25.4660
1	9	0	25.4425	26.5129
1	10	0	20.6299	26.2672
1	11	0	19.4859	22.1355
1	0	1	63.8865	52.2500
1	1	1	24.2738	21.8470
1	2	1	39.1746	29.4413
1	3	1	66.2069	70.9129
1	4	1	26.4379	26.7412
1	5	1	21.2909	20.7865
1	6	1	36.6839	36.9053
1	8	1	26.3063	27.5496
1	9	1	24.3373	27.8898
1	10	1	8.1733	10.2581
1	0	2	68.2750	59.3781
1	1	2	24.7320	24.1094
1	2	2	75.3756	68.9250
1	3	2	61.6172	50.3662
1	4	2	18.5416	17.0958
1	5	2	32.5384	32.9250
1	6	2	26.7537	27.3189
1	7	2	21.3156	21.2620
1	8	2	25.7103	26.8856
1	9	2	11.3606	11.7909
1	10	2	6.9225	7.4158
1	0	3	22.5555	19.7992
1	1	3	41.8046	44.2826
1	2	3	62.6280	63.6521
1	3	3	38.7226	33.5483
1	4	3	48.1064	42.3737
1	5	3	44.0631	45.0682
1	6	3	19.3745	19.4349
1	7	3	14.5324	15.5065
1	8	3	34.5632	36.6502
1	9	3	32.6638	34.2674
1	10	3	12.2507	13.4074
1	1	4	18.6701	19.9259
1	2	4	22.8760	24.2339
1	3	4	35.1839	35.9335
1	4	4	33.7505	33.9473
1	5	4	16.8822	17.0267
1	6	4	11.2584	10.9854
1	7	4	9.9132	8.2829
1	8	4	13.4117	12.7240
1	9	4	12.0572	12.9758
1	2	5	14.1361	17.0595
1	3	5	28.8543	29.1162
1	4	5	18.3482	18.1848
1	7	5	16.0726	18.5171
1	8	5	11.4798	13.4556
1	3	6	27.0307	30.3046
1	4	6	8.2739	9.6389
1	5	6	16.8776	18.6624
1	6	6	11.6671	13.2266
1	0	7	15.5324	19.9154
1	1	7	15.1098	17.6998
2	1	0	33.2886	29.9450
2	2	0	68.8114	73.4050
2	3	0	49.9684	52.2140
2	4	0	58.5638	53.2560
2	5	0	16.0533	11.8060
2	6	0	32.9955	30.9424
2	8	0	28.6999	33.7177
2	9	0	25.6366	30.4077
2	10	0	12.8769	16.2578
2	11	0	16.2207	17.5242
2	0	1	18.3197	15.8529
2	1	1	35.5354	25.7260
2	2	1	120.4336	93.9857
2	3	1	71.7673	72.6806
2	4	1	62.8272	66.3174
2	5	1	39.2463	41.6624
2	6	1	22.9069	24.2032
2	7	1	19.5855	19.4818
2	8	1	31.9153	37.0513
2	9	1	17.3386	9.9905
2	10	1	10.3607	12.1020
2	11	1	11.9503	14.0743
2	1	2	55.4251	47.0318
2	2	2	20.0711	15.0362
2	3	2	47.8555	35.2929
2	4	2	11.2064	7.9721
2	5	2	14.2725	15.0498
2	7	2	24.9626	28.7640
2	8	2	14.8740	15.1967
2	9	2	16.1872	18.9843
2	10	2	8.6372	10.6073
2	0	3	14.9047	13.2544
2	1	3	28.6092	28.4363
2	2	3	36.8752	35.8526
2	3	3	101.0282	92.7520
2	4	3	21.3481	15.5754
2	5	3	14.1399	13.1550
2	6	3	27.6909	29.1060
2	7	3	12.5350	12.8895
2	8	3	18.5234	20.1033
2	9	3	32.2182	38.6684
2	10	3	13.8189	16.4904
2	0	4	30.2337	28.8238
2	1	4	14.5949	14.2695
2	2	4	22.6418	21.1842
2	3	4	14.9131	12.9929
2	4	4	24.3081	20.5597
2	6	4	15.0331	17.4684
2	8	4	26.5187	30.8403
2	9	4	11.8121	14.8393
2	0	5	14.6758	17.3047
2	1	5	14.0799	18.7525
2	2	5	46.1906	50.6287
2	3	5	27.5458	29.4005
2	4	5	21.7584	23.4352
2	5	5	14.1441	18.7828
2	6	5	7.4468	10.0082
2	7	5	13.3291	16.1334
2	1	6	30.0704	35.7490
2	2	6	14.7847	16.5818
2	3	6	21.0368	25.3966
2	4	6	16.1956	19.9412
2	5	6	22.8539	28.7366
3	1	0	53.9266	61.9810
3	5	0	35.3028	38.3848
3	6	0	11.8822	9.9527
3	7	0	35.5029	37.6595
3	10	0	9.3557	7.4968
3	11	0	25.2466	22.8502
3	0	1	31.5880	36.1755
3	1	1	87.9473	108.1566
3	2	1	17.6232	19.9518
3	3	1	10.8879	11.5285
3	4	1	11.9760	12.7437
3	5	1	68.7732	69.8341
3	6	1	21.1566	20.5092
3	7	1	26.3473	24.8488
3	8	1	29.8870	26.3893
3	10	1	10.3688	3.3064
3	0	2	64.1203	68.6895
3	1	2	27.1290	31.1299
3	2	2	15.0529	15.9055
3	3	2	34.8275	35.3026
3	4	2	11.7697	14.9280
3	5	2	15.8784	16.1730
3	6	2	42.1694	38.9081
3	7	2	17.6045	14.7290

Table A (continued)

h	k	l	$\lvert Y_{obs} \rvert$	$\lvert Y_{calc} \rvert$
3	9	2	19.1116	14.7922
3	10	2	16.4976	14.2387
3	0	3	114.3634	126.0576
3	1	3	31.2253	31.3534
3	2	3	38.1295	38.6231
3	3	3	52.1193	50.5991
3	4	3	43.7204	41.6704
3	6	3	78.8793	70.6084
3	7	3	37.3790	34.8667
3	9	3	24.6150	20.9102
3	10	3	18.1173	15.0890
3	1	4	11.2318	14.3257
3	2	4	19.2742	18.1108
3	3	4	26.3723	27.6094
3	4	4	21.7758	19.8071
3	5	4	19.1242	18.1003
3	6	4	27.4417	24.8290
3	7	4	14.8090	13.2183
3	8	4	12.9329	9.3979
3	9	4	13.9835	12.3557
3	0	5	34.0020	37.9609
3	1	5	41.4940	43.5483
3	2	5	28.9426	29.7510
3	3	5	13.1080	9.0806
3	4	5	22.2260	21.3797
3	5	5	38.8049	35.1463
3	6	5	25.5156	24.0298
3	7	5	26.6850	22.4615
3	0	6	21.8696	23.4185
3	1	6	10.7816	13.3046
3	2	6	17.0291	18.0112
3	3	6	14.1586	14.0719
3	4	6	18.5488	15.4712
3	5	6	9.7059	8.5658
4	1	0	15.3211	17.0492
4	2	0	72.3168	83.3924
4	3	0	23.3038	26.1405
4	4	0	24.0982	24.9656
4	5	0	33.6475	36.6728
4	6	0	25.0148	26.2468
4	7	0	11.9380	10.1559
4	8	0	41.5135	44.6777
4	9	0	33.4752	33.3693
4	10	0	10.0381	10.3708
4	0	1	11.1214	11.7240
4	1	1	24.4370	26.2035
4	2	1	15.3711	17.7373
4	3	1	36.4695	39.9329
4	4	1	17.0320	17.4591
4	5	1	29.6866	30.4982
4	6	1	25.6370	25.1453
4	7	1	19.0041	19.9239
4	8	1	16.9432	13.8035
4	9	1	13.9545	11.1847
4	0	2	24.9926	25.2430
4	1	2	23.8704	20.5815
4	2	2	14.3434	12.7291
4	3	2	45.8132	46.2433
4	4	2	30.4533	31.3538
4	5	2	17.7487	15.5770
4	6	2	24.9426	23.1528
4	8	2	16.3877	13.5757
4	9	2	33.0142	31.3779
4	10	2	25.0426	23.5159
4	0	3	15.8099	17.6648
4	1	3	17.2431	19.0997
4	2	3	32.3364	32.3752
4	4	3	35.1640	34.4399
4	5	3	30.3921	28.5365
4	6	3	33.0697	31.1376
4	7	3	10.3048	9.8001
4	8	3	20.5873	19.9881
4	0	4	41.7135	39.7011
4	1	4	31.7587	33.0351
4	3	4	27.1202	24.6660
4	4	4	16.5599	15.5626
4	5	4	28.9589	27.6726
4	6	4	25.8480	21.9522
4	7	4	9.3548	11.4134
4	8	4	6.8050	7.1642
4	0	5	14.2323	16.2981
4	1	5	12.5213	13.6498
4	2	5	10.3326	10.2113
4	3	5	8.7827	9.1824
4	4	5	24.4093	23.2498
4	5	5	15.6210	14.7371
4	6	5	14.0267	13.6325
4	7	5	18.2375	16.8976
4	0	6	21.3206	24.0576
4	1	6	18.7375	18.7229
4	2	6	9.9937	8.2253
4	3	6	13.4379	10.8010
4	5	6	28.2701	26.0047
5	1	0	69.9978	75.1604
5	2	0	31.6834	33.7817
5	3	0	115.0375	127.1195
5	4	0	17.8766	19.3059
5	5	0	36.9264	39.7062
5	6	0	14.3777	14.7476
5	7	0	31.0496	32.0897
5	8	0	20.1602	20.0789
5	9	0	47.2867	49.1266
5	1	1	27.2365	26.1387
5	3	1	19.1546	19.6133
5	4	1	28.4202	29.2241
5	5	1	27.2522	27.0766
5	6	1	8.2390	5.5638
5	7	1	12.6650	13.6785
5	8	1	22.5382	23.0075
5	9	1	23.9786	23.0273
5	10	1	11.9841	12.2983
5	1	2	10.8789	9.0679
5	2	2	89.9171	89.1864
5	3	2	40.2210	38.4977
5	4	2	48.2976	48.0741
5	5	2	10.8317	11.9363
5	7	2	19.3117	17.2920
5	8	2	45.5478	43.4981
5	9	2	14.2101	13.6413
5	10	2	9.0928	8.7653
5	0	3	41.1795	41.6062
5	1	3	18.7932	18.5290
5	2	3	12.7121	12.6846
5	3	3	20.2650	19.2024
5	4	3	23.3920	23.1210
5	5	3	10.3289	6.9367
5	6	3	26.5399	26.3517
5	7	3	16.2948	16.4286
5	8	3	10.9889	7.9818
5	9	3	16.8395	15.7314
5	0	4	11.1931	9.7654
5	1	4	26.3984	27.5737
5	2	4	29.4730	26.9537
5	3	4	14.6029	16.2652
5	4	4	32.1443	30.1097
5	5	4	27.6293	26.2558
5	7	4	10.2713	10.4942
5	8	4	13.6654	13.5802
5	0	5	21.9620	22.3848
5	1	5	13.5449	14.9199
5	4	5	6.5263	7.0901
5	5	5	8.3071	6.5120
5	6	5	16.2005	14.8376
5	0	6	39.2886	40.9459
5	1	6	15.2629	11.9366
5	2	6	28.2264	27.9534
5	3	6	33.5585	33.3303
5	4	6	29.6563	29.2325
6	2	0	27.0231	27.8246
6	3	0	35.7169	37.3693
6	4	0	29.1978	29.2302
6	6	0	34.6102	35.8629
6	7	0	28.0862	29.0371
6	8	0	5.8493	0.2574
6	9	0	34.0180	36.5112
6	10	0	11.0820	11.9442
6	0	1	42.2943	40.9098
6	1	1	24.2417	23.7044
6	2	1	20.2418	20.3011
6	3	1	52.2842	53.8390
6	4	1	12.8538	13.9511
6	6	1	38.4207	39.0216
6	7	1	28.7512	27.5991
6	8	1	11.5286	11.3615
6	9	1	10.8927	12.0743
6	0	2	22.0913	20.9174
6	1	2	44.2699	43.1866
6	2	2	24.9989	24.7294
6	3	2	6.8395	9.4219
6	4	2	15.5624	15.1985
6	5	2	34.4014	32.9080
6	6	2	15.7954	14.0278
6	7	2	11.6937	12.8263
6	8	2	24.9455	23.3160
6	0	3	35.6829	35.5024
6	4	3	26.7901	26.2057
6	5	3	37.5469	35.2431
6	6	3	23.4213	23.8619
6	7	3	26.4600	24.8254
6	8	3	20.6545	21.0712
6	9	3	5.9172	6.1674
6	0	4	20.5428	20.2212
6	1	4	26.2853	26.2915
6	2	4	12.0286	12.4611
6	3	4	17.9313	17.1199
6	5	4	18.5914	18.0258
6	6	4	13.5285	12.7638
6	7	4	11.6548	12.1986
6	0	5	38.2945	38.9185
6	1	5	15.3731	16.7967
6	4	5	6.6648	9.8498
6	5	5	10.3539	8.5727

Table A (continued)

h	k	l	$\lvert Y_{obs}\rvert$	$\lvert Y_{calc}\rvert$	h	k	l	$\lvert Y_{obs}\rvert$	$\lvert Y_{calc}\rvert$	h	k	l	$\lvert Y_{obs}\rvert$	$\lvert Y_{calc}\rvert$
6	6	5	24.7077	24.0021	7	2	4	10.9773	10.6848	9	2	2	14.0564	14.4235
6	0	6	19.8050	20.7745	7	3	4	20.4833	19.2663	9	3	2	21.5124	20.1388
6	1	6	9.9025	11.5095	7	4	4	10.1796	10.0711	9	4	2	8.2672	6.8527
6	2	6	19.8390	19.6299	7	5	4	21.1473	20.4975	9	5	2	6.9373	7.4925
6	3	6	18.6788	19.0022	7	6	4	18.3051	18.1363	9	7	2	23.8573	23.8082
7	1	0	31.1263	31.9690	7	7	4	15.1332	14.6130	9	1	3	12.2700	11.3670
7	2	0	6.6399	7.2690	7	0	5	11.2735	11.9747	9	2	3	13.7993	13.3825
7	3	0	42.9873	43.6142	7	1	5	18.8449	19.6329	9	4	3	8.2672	7.9110
7	4	0	9.9598	9.6708	7	3	5	7.2179	8.1277	9	5	3	14.9075	15.2353
7	5	0	28.1646	29.3592	7	5	5	20.5024	20.8110	9	6	3	14.5751	13.8084
7	6	0	24.8542	25.6897	7	0	6	16.6093	17.5226	9	1	4	15.7586	16.0993
7	7	0	10.6811	11.1755	7	1	6	7.6335	9.6106	9	2	4	14.1850	15.1571
7	8	0	8.4073	8.8289	8	1	0	21.7434	22.0278	9	3	4	24.0746	24.3563
7	9	0	26.3064	27.2884	8	2	0	31.3510	31.3327	9	4	4	14.0387	14.8068
7	0	1	24.4720	23.5274	8	3	0	7.8671	8.2273	9	5	4	7.3407	7.0516
7	1	1	42.1657	41.3492	8	4	0	12.5926	11.5079	9	0	5	6.4586	5.6876
7	2	1	14.5122	15.0826	8	5	0	14.7030	13.3510	9	1	5	7.6688	8.1820
7	3	1	18.3910	18.4564	8	6	0	15.7386	17.3866	9	2	5	10.3595	11.5833
7	4	1	23.3256	22.4269	8	7	0	17.2572	18.2241	10	1	0	6.6086	6.7016
7	5	1	31.2552	31.8860	8	8	0	17.5922	19.6236	10	2	0	29.1700	28.6706
7	6	1	19.1697	19.4682	8	1	1	16.6741	16.0597	10	4	0	31.9007	30.6591
7	7	1	12.2766	14.6377	8	2	1	44.3135	44.4727	10	5	0	26.0119	24.6538
7	8	1	12.1381	11.7807	8	3	1	12.2445	10.2050	10	0	1	8.1737	9.7493
7	9	1	12.9645	12.7992	8	4	1	31.3118	30.6401	10	1	1	23.5459	23.1826
7	1	2	25.8526	24.3569	8	6	1	15.0467	15.1244	10	2	1	19.3708	19.2766
7	2	2	26.4306	25.3596	8	7	1	6.9142	5.9270	10	3	1	4.8067	4.3596
7	3	2	10.5999	8.2653	8	8	1	23.8581	24.8138	10	4	1	13.7235	13.7850
7	4	2	18.5773	17.1803	9	1	0	31.5217	30.7551	10	5	1	15.2839	15.0518
7	5	2	20.3209	18.8469	9	2	0	29.7751	30.4430	10	0	2	5.7262	7.9123
7	6	2	18.5439	17.9474	9	4	0	14.6371	15.3302	10	1	2	34.9752	33.2907
7	7	2	20.7508	20.6201	9	5	0	31.2956	31.8082	10	2	2	11.7404	11.4434
7	8	2	11.7177	11.8051	9	6	0	18.7330	19.2563	10	3	2	9.5716	9.0948
7	9	2	7.2800	6.6350	9	7	0	19.2295	19.8984	10	4	2	17.6571	15.7658
7	0	3	54.3085	55.1434	9	8	0	22.0133	22.9413	10	6	2	7.2960	7.1780
7	1	3	12.7304	11.7329	9	0	1	23.1836	22.1338	10	0	3	10.8302	9.6499
7	3	3	16.8290	16.8060	9	1	1	9.8674	9.2513	10	1	3	8.1877	7.9274
7	4	3	10.5235	11.1179	9	2	1	13.6974	12.9977	10	2	3	23.3648	23.2821
7	5	3	31.0689	30.1213	9	3	1	20.9760	19.7304	10	3	3	26.4020	26.8220
7	6	3	32.0721	32.4377	9	4	1	23.7244	23.9665	10	0	4	9.7713	10.7887
7	7	3	8.2975	9.1289	9	6	1	7.7219	8.5336	10	1	4	12.4974	13.4411
7	8	3	15.8975	15.0792	9	7	1	4.6899	3.5756	10	3	4	5.9027	7.6840
7	0	4	13.8960	15.0598	9	8	1	17.3677	18.6772	10	4	4	5.1504	7.2983
7	1	4	18.9595	17.8901	9	1	2	18.2587	18.3092					

Comparing the NQR results with the crystal structure, we expect a relation between the direction of the main components of the EFG tensor and the bond directions. In Fig. 12, one of the $AlCl_4^{\ominus}$ tetrahedra of the unit cell is shown with its next neighbors of $Na^{\oplus}$ ions.

No simple relation seems to exist between the direction cosines of the EFG tensor at the site of ^{23}Na and the coordination of the $Na^{\oplus}$ ions within the lattice of $NaAlCl_4$. The bond character of sodium in solid $NaAlCl_4$ is a purely ionic one in which case the multipoles surrounding the ion considered are solely responsible for the EFG at its site. Therefore, only extended calculations of the EFG on the basis of a multipole model will yield the magnitude and orientation of the tensor components at the site of the sodium ion.

A somewhat different situation is found for the EFG tensors at the site of ^{27}Al and ^{35}Cl respectively within the tetrahedron $AlCl_4^{\ominus}$. Here, by an application of the Townes-Dailey theory[28] in its simplest form to the NQR data, a mean covalent character of about 20% is calculated for the Al – Cl bond. From this one expects that the Al – Cl bond should be responsible for most of the EFG at the sites of both atoms Cl and Al, respectively.

Applying this assumption to the EFG at the site of ^{27}Al, a qualitative comparison with the experimental data is not possible.

In a first approximation, the ion $AlCl_4^{\ominus}$ is a tetrahedron, and then from symmetry considerations it follows that the intraionic EFG at the Al site is zero. The nuclear quadrupole coupling constant found in the experiment is therefore due to a) the slight distortion of the tetrahedron which disturbs the total compensation of the intraionic components of the EFG, and b) the external charges (rest of the lattice), the crystal field.

Preliminary calculations of the EFG at the sites of ^{27}Al ions based on a multipole model have turned out to be insufficient to explain the magnitude and orientation of the EFG. Extensive calculations are probably necessary to solve the problem.

Considering the EFG at the sites of the chlorines the Al – Cl bond is determining the orientations of the EFG tensors. In Table 10 the angles between the crystal axes and the bond directions Al – Cl are compared with the angles between the crystal axes and the directions of the *z*-axes of the ^{35}Cl EFGs. It can be seen that the main axes V_{zz} are collinear with the bond directions Al – Cl within the limits of error. The asymmetry parameters η found for ^{35}Cl in $NaAlCl_4$ are in the range $18\% \leqq \eta \leqq 32\%$ and the coupling constants $|e^2 q Q/h|$ (^{35}Cl) are between 21.6 MHz and 23.0 MHz. The rather small spread in V_{zz} is in accordance with the small deviations of the bond lengths Al – Cl from the mean values ($d(\overline{\text{Al}-\text{Cl}}) = 2.13 \pm 0.01$ Å). The spread of η is considerable. It is due to the influence of the external charges on the EFG tensor, to the interactions between the Cl ions within one $AlCl_4^{\ominus}$ tetrahedron, and to the anisotropic thermal vibrations of the Cl ions.

While the orientations of the EFG tensors with respect to the crystallographically equivalent sites of the atoms are resolved for the chlorine atom in $NaAlCl_4$, the questions remain open for the sodium and aluminum in this lattice. Extended lattice summations on the basis of a multipole model will be done and should be helpful to solve the problem quantitatively.

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[1] A. Weiss and K. Zohner, Phys. Stat. Sol. **21**, 257 [1967].

[2] N. C. Baenziger, Acta Cryst. **4**, 216 [1951].

[3] J. Kendall, E. D. Crittenden, and H. K. Miller, J. Amer. Chem. Soc. **45**, 963 [1923].

[4] A. Chrétien and E. Lous, Compt. Rend. Acad. Sci. Paris, Ser. C **217**, 451 [1943].

[5] W. Fischer and A. L. Simon, Z. anorg. allg. Chem. **306**, 1 [1960].

[6] E. Paschalis, Diplomarbeit, Darmstadt 1963.

[7] W. Scheinert, Diplomarbeit, Darmstadt 1970.

[8] R. R. Richards and N. W. Gregory, J. Physic. Chem. **69**, 239 [1965].

[9] A. Weiss, Z. Naturforsch. **15 a**, 536 [1960].

[10] G. M. Volkoff, H. E. Petch, and D. W. L. Smellie, Can. J. Phys. **30**, 270 [1952]; G. M. Volkoff, Can. J. Phys. **31**, 820 [1953].

[11] J. D. Cuthbert and H. E. Petch, J. Chem. Phys. **38**, 1912 [1963].

[12] J. D. Cuthbert and H. E. Petch, J. Chem. Phys. **39**, 1247 [1963].

[13] L. C. Lal and H. E. Petch, J. Chem. Phys. **40**, 2741 [1964].

[14] J. C. Evans and G. Y.-S. Lo, Inorg. Chem. **6**, 836 [1967].

[15] D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, Inorg. Chem. **13**, 1471 [1974].

[16] V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 [1951].

[17] C. Dean, Thesis, Harvard University 1952.

[18] W. Scheinert, Dissertation, Darmstadt 1973.

[19] Timm Deeg and Alarich Weiss, Ber. Bunsenges. physik. Chem. **79**, 497 [1975].

[20] D. J. Merryman, J. D. Corbett, and P. A. Edwards, Inorg. Chem. **14**, 428 [1975].

[21] E. R. Andrew, R. G. Eades, J. W. Hennel, and D. G. Hughes, Proc. Phys. Soc. **79**, 954 [1962].

[22] A. Weiss and D. Biedenkapp, Z. Naturforsch. **17 a**, 794 [1962].

[23] A. Weiss and W. Weyrich, Z. Naturforsch. **24 a**, 474 [1969].

[24] G. E. Peterson and P. M. Bridenbaugh, J. Chem. Phys. **51**, 2610 [1969].

[25] S. Ketudat, I. Berthold, E. Paschalis, and Alarich Weiss, Magnetic Resonance and Reaction, Proc. XIVth Colloque Ampère, Lubljana 1966, North Holland Publ. Co. 1967, p. 1119.

[26] N. Weiden and A. Weiss, J. Magnetic Resonance **20**, 279 [1975].

[27] A. Weiss and A. Wüst, unpublished results.

[28] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 [1949].