

Superposition-Model Analysis of NQR Data for NaAlCl₄

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The quadrupole splitting patterns for ²³Na and ²⁷Al in NaAlCl₄ can very satisfactorily be reproduced by the distortions of their first coordination spheres, as shown by application of the superposition model. The same exponent of 7 for the dependence on bond lengths was used as previously found for NMR data of ⁹Be, ²³Na, ²⁵Mg, ²⁷Al and ²⁹Si with oxygen as ligand. The intrinsic splitting parameters are in the same range, perhaps a little larger than for oxygen as ligand. Small deviations between observed and calculated splitting patterns just outside the limits of error of the crystal structure data may be due to influences of the lattice, especially in the case of ²⁷Al, for which the distortions are fairly small.

Introduction

Purely electrostatic mechanisms are of minor importance for the zero-field splittings (ZFSs) of transition-metal ions in solids, whereas the more important influences of overlap and covalency are obtained as sums of axially symmetric contributions of the nearest neighbors (ligands) of these ions, as the experimental success [1] of the superposition model (SPM) [2] has shown. Similarities in the nuclear quadrupole (NQR) splitting patterns of ²⁷Al and ZFS patterns of Fe³⁺ in the same sites in minerals [3] as well as the observation that the ²⁷Al NQR splitting patterns in a feldspar are better reproduced by the influences of their oxygen ligands alone than by a lattice summation [4] suggest that the SPM may also be applicable to anisotropies of NMR data. Indeed it could be shown that the chemical shift anisotropies of ²⁹Si in Mg₂SiO₄ [5] and of ²⁰⁵Tl and ²⁰⁷Pb in TIPbI₃ [6] as well as the NQR splitting patterns of ²⁵Mg in Mg₂SiO₄ [5] can be very well reproduced by the distortions of their MX_n coordination polyhedra obtained by application of the SPM. The high exponents for the dependences of these distortions on bond lengths required for these fits are an indication that also in these cases electro-

static mechanisms are of minor importance. A more systematic evaluation of NQR data for ²⁷Al in minerals [7] resulted in the same exponent of 7 as previously found for the light nuclei ²⁵Mg and ²⁹Si and showed very good agreements in cases of large distortions, whereas for small quadrupole coupling constants below about 3 MHz larger deviations were found. They can be attributed to significant contributions of the lattice, which were also postulated in a recent theoretical investigation [8]. Satisfactory agreement was also obtained for the chemical shift anisotropies of ¹¹¹Cd in synthetic crystals [9] and, like in the case of the heavy nuclei ²⁰⁵Tl and ²⁰⁷Pb, much higher exponents for the dependence on bond lengths were needed than in the cases of light nuclei.

In all these cases only systems with oxygen as ligand were studied. For the ZFSs of transition-metal ions a very marked dependence on the type of ligand was observed [1], which can be regarded as an important experimental indication for the prevailing mechanism(s). Unfortunately the signs of the NQR splittings (quadrupole coupling constants), i.e. the energetic orders of the split levels are not known experimentally because their determination would require measurements of relative intensities at extremely low temperatures. This sign changes for the ZFSs of Mn²⁺ and Fe³⁺ with increasing atomic number of the ligands [1]. Nevertheless, the change of the absolute values of the intrinsic NQR splitting parameters with the type of

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ligand is also an important information, and as a first contribution towards their evaluation we here report results for Cl^- as ligand in NaAlCl_4 , for which NQR data are known [10].

Results

The NQR splitting as a purely quadrupolar quantity is completely equivalent to the ZFS. Therefore the SPM can be applied in the same way with the following equivalences:

$$C \equiv e^2 q Q/h \cong b_2^0 \quad \text{and} \quad \eta \cong b_2^2/b_2^0.$$

Thus the intrinsic NQR parameter \bar{C} (=NQR splitting per unit distortion, where distortion is the effective fraction of a ligand at normal bond distance) is obtained from

$$\bar{C} = 2C/\sum_i (3 \cos^2 \vartheta_i - 1) \left(\frac{R_0}{R_i} \right)^t = C/d_{zz} \quad (1)$$

with ϑ_i the angle between the $\text{M}-\text{Cl}_i$ bond direction and the z axis, $t=7$ taken from the previous results for the same nuclei [7], and $R_0=282$ pm for $\text{Na}-\text{Cl}$ and 213.5 pm for $\text{Al}-\text{Cl}$. Thus d_{zz} is the distortion along the z axis, the maximum principal value, and thus is a dimensionless quantity.

Equation (1) can only be applied if the calculated and experimental orientations of the principal axes at least approximately coincide. In order to test this condition the directions of the principal axes of the distortion were calculated according to

$$d_{jk} = \frac{1}{2} \sum_i (3 \cos^2 \Theta_i - 1) \left(\frac{R_0}{R_i} \right)^7, \quad (2)$$

where Θ_i are the angles between the $\text{M}-\text{Cl}_i$ bond directions and the direction under consideration (index jk).

Due to the triclinic point symmetries for both Al and Na, none of these principal axes should coincide with a crystal axis, and therefore the results are best reproduced for these axes directions in stereographic projections. These are shown in Figs. 1 and 2 for ^{27}Al and ^{23}Na , respectively, where the crystal structure data are available from the same source as the NQR data [10]. In both cases the experimental and calculated directions do not coincide within the limits of error of the crystal structure data, but are sufficiently close to allow calculation of the intrinsic NQR

parameters from the data for the z axis:

$$|\bar{C}| = 1.4895 (12)/0.140 (32) \\ = 11.2 (2.6) \text{ MHz/distortion for } ^{27}\text{Al},$$

$$\text{and } |\bar{C}| = 1.1117 (12)/0.788 (24) \\ = 1.41 (4) \text{ MHz/distortion for } ^{23}\text{Na}.$$

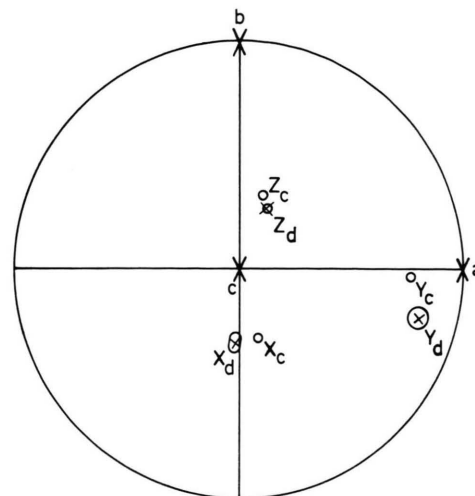


Fig. 1. Stereographic projection showing the principal axes directions of the NQR splitting for ^{27}Al in NaAlCl_4 (○) and those calculated from the crystal structure data according to (2) (x with closed loops for the limits of error) for one of the four magnetically nonequivalent sites. The experimental positions are seen to be close to the calculated ones, but just outside the limits of error of the latter, thus indicating an at least approximate validity of the SPM.

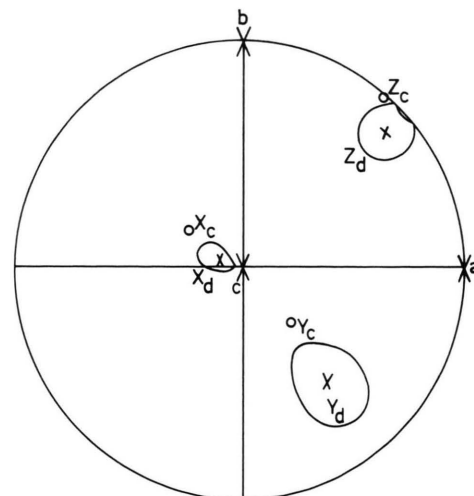


Fig. 2. Same comparison of principal axes directions with analogous symbols as in Fig. 1, but for ^{23}Na in NaAlCl_4 . Again the experimental points are just outside the (significantly larger) limits of error. All signs of the direction cosines for the y direction had to be inverted (change from angle ϑ to $180-\vartheta$) to obtain better agreement for this direction.

Table 1. Principal values of the site distortions and their direction cosines (for one of the four magnetically nonequivalent sites).

	Distortion	Direction cosines			
		<i>a</i>	<i>b</i>	<i>c</i>	
<i>z</i>	−0.140 (32)	0.2540	0.6621	0.7051	²⁷ Al
<i>y</i>	0.132 (20)	−0.9650	0.2223	0.1389	
<i>x</i>	0.007 (33)	−0.0647	−0.7157	0.6954	
<i>z</i>	0.788 (24)	0.1950	0.7264	0.6591	²³ Na
<i>y</i>	−0.506 (20)	−0.9655	−0.0238	−0.2595	
<i>x</i>	−0.282 (15)	0.1728	−0.6869	0.7057	

For ²³Na a change of the angles for the *y* direction from ϑ to $180 - \vartheta$ was necessary to obtain good agreement, but experimentally no distinction between these two directions is possible.

A further test for the applicability of the SPM besides the agreement of the experimental and calculated principal axes directions is the degree of agreement of the asymmetry parameters η . In both cases the experimental values are smaller than the calculated ones:

	Observed	Calculated
²⁷ Al:	0.3375 (11)	1.06 (58)
²³ Na:	0.2153 (5)	0.28 (4)

Whereas for ²³Na it is again just outside the limits of error, for ²⁷Al significantly larger values are calculated. Those above unity suggest an interchange of the *z* and *y* axes, but the value of 0.89 obtained from the average crystal structure data is in agreement with the experimental order of axes.

Discussion

Undoubtedly the experimental and calculated splitting patterns are so similar that also in this case the distortions of the first coordination spheres account

for the larger part of the NQR splittings, but on the other hand the deviations outside the limits of error indicate that other contributions cannot be ignored. Undoubtedly, still better agreements could have been obtained if the exponents *t* were optimized individually for these systems. However, it is doubtful whether such a procedure would be of physical significance. The large number of published results for ²⁷Al [5] clearly indicate that for this nucleus the value of 7 is at least close to the optimum, and there is no reason to assume that it should be significantly different for a nucleus with a very similar number of nucleons like ²³Na. These previous results for ²⁷Al also suggest that the observed deviations are due to contributions of the lattice as a result of the fairly small value of *C* and the small distortions evident from Table 1. The value of the intrinsic NQR parameter \bar{C} is almost 50% larger than the average of 7.8 MHz/distortion obtained for oxygen coordination. This may be due to the higher covalency of the Al–Cl bonds and/or to the higher spin-orbit coupling constant of the heavier Cl ligands. However, this value is still within the range of values observed for oxygen as ligand. For ²³Na only the value of *C* = 1.96 MHz/distortion for natrolite has been reported [5]. From NQR and crystal structure data for NaNO₃ [11, 12] and NaClO₃ [13, 14] values of \bar{C} only about half as large are obtained. Thus we can only conclude that the absolute values of the intrinsic NQR parameters for Cl as ligand are similar, possibly slightly larger than for oxygen. More experimental NQR data for chlorides as well as for behavior and still less electronegative ligands like Br, I, or Se and Te would be desirable to test the validity of the SPM further and to determine the dependence of the intrinsic NQR parameter on the type of ligand in case of its applicability.

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