# Electric Quadrupole Interaction of $^{20}F$ in a $KZnF_3$ Single Crystal

H. Ackermann, D. Dubbers, M. Grupp, P. Heitjans, and H.-J. Stöckmann
Physikalisches Institut der Universität Heidelberg and
Institut Laue-Langevin, Grenoble

K.-P. Wanczek
Institut für Physikalische Chemie der Universität Frankfurt

K. Recker and R. Leckebusch
Mineralogisches Institut der Universität Bonn

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Nuclear magnetic resonance measurements were carried out on neutron activated $^{20}F$ ($T_{1/2} = 11$ s) nuclei in a single crystal of $KZnF_3$. The quadrupolar splitted NMR spectrum, detected via the $^{20}F$ $\beta$-radiation asymmetry, could be observed using a radio frequency modulation technique. The quadrupole coupling constant was determined to $e^2 q Q/h = +(12.0 \pm 1.5)$ MHz at room temperature. The sign of $e^2 q Q$ was obtained from a simultaneous $\gamma$-ray anisotropy measurement on the succeeding $^{20}Ne$ transition. Utilising a calculated field gradient of the fluorine atom, an $f_Q = 4.6\%$ is determined. This value is compared with literature data of similar compounds.

## 1. Introduction

Fluorine is the only halogen which has no stable isotope with nonvanishing quadrupole moment. Therefore classical nuclear quadrupole resonance in fluorine compounds is not possible. Until recently the measurement of fluorine quadrupole coupling constants was only possible by observing the excited 197 keV-state of $^{19}F$ ($T_{1/2} = 87$ ns) in perturbed $\gamma$-angular correlation experiments[1–3]. Since the 197 keV-state is populated via a (p, p′)-reaction by protons of several MeV, in these experiments a lot of lattice defects is produced. Haas et al.[3] recently studied the transition metal fluorides $KMF_3$ (M = Ni, Co, Mn) and $RbMnF_3$. In these cases strong radiation damage appeared only at temperatures substantially lower than room temperature, where the defects are frozen.

This paper reports the measurement of the fluorine quadrupole coupling constant at room temperature in the metal fluoride $KZnF_3$ using the radioactive isotope $^{20}F$ ($T_{1/2} = 11$ s) in an in-beam nuclear magnetic resonance (NMR) experiment. Polarized $^{20}F$ nuclei are produced in their ground state by capture of polarized, thermal neutrons:

$$^{19}F + n_p \rightarrow {}^{20}F_p^* \xrightarrow{\gamma's} {}^{20}F_p \xrightarrow{\beta} {}^{20}Ne^* \xrightarrow{\gamma} {}^{20}Ne\,.$$

The nuclear polarization of the $^{20}F$ nuclei can be detected via their asymmetrically distributed $\beta$-radiation. The induction of NMR transitions appears as reduction of this $\beta$-decay asymmetry. For details of the methods see[4, 5].

In this type of experiment there is a certain risk of defect production, too, because the activation process passes the excited compound state $^{20}F^*$. It deexcites in about 1 ps via a cascade which imparts to the $^{20}F$ nuclei an average recoil energy of several 100 eV. By this the activated nuclei may be displaced up to some lattice constants and only few point defects are produced. In $CaF_2$, e. g., they exhibit a well defined structure and anneal far below room temperature[6]. Fast annealing processes do not disturb the measurements because of the relatively long lifetime of the $^{20}F$ nuclei representing also the time for their observation.

## 2. Energy Levels

$KZnF_3$ has a cubic perewskite-like structure with the lattice constant $a = 4.055$ Å[7]. The unit cell contains one molecule, the positions of the ions are (Figure 1):

K: (1/2, 1/2, 1/2); F1: (1/2, 0, 0);
Zn: (0, 0, 0); F2: (0, 1/2, 0);
F3: (0, 0, 1/2).

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Reprint requests to Prof. Dr. H. Ackermann, Physikalisches Institut der Universität Heidelberg, Philosophenweg 12, *D-6900 Heidelberg 1.*

Each fluorine ion sits on a fourfold symmetry axis parallel to a principal axis of the crystal, the plane perpendicular to this axis is a mirror plane (see Figure 1). By this, the fluorine nucleus sees an axially symmetric field gradient tensor with the principal axis parallel to one of the crystal axes. The orientation of our KZnF$_3$-single crystal has been chosen with a [111]-axis parallel to the external field. In this case the angle between the principal axis of the field gradient tensor and the external field is the same for all the fluorine ions, namely $\vartheta = 54.7°$.

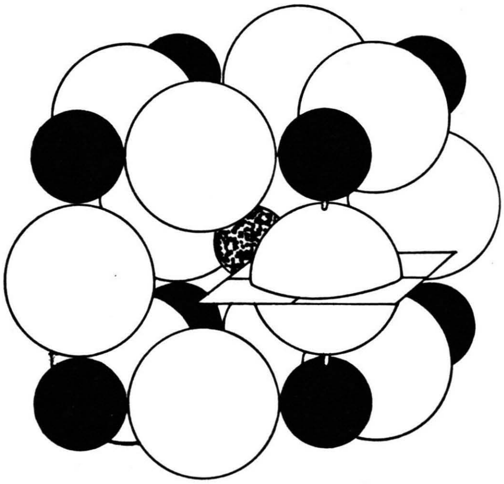

Fig. 1. Crystal structure of KZnF$_3$, speckled sphere: K$^+$ ion, black spheres: Zn$^{++}$ ions, white spheres: F$^-$ ions. The radii of the spheres do not correspond to the true radii of the ions. For one F$^-$ ion the mirror plane and the fourfold symmetry axis are indicated.

By an external magnetic induction $B_0$ the $(I=2)$-ground state of $^{20}$F is split into its five m-sublevels

(i) by the magnetic Zeeman interaction $\mathcal{H}_\mathrm{M} = -g_I\,\mu_K \cdot B_0 \cdot I_z$ and

(ii) by the electric quadrupole interaction $\mathcal{H}_\mathrm{E} = (e^2\,q\,Q/24)\exp\{-i\,\vartheta\,I_y\}(3\,I_z^2 - I^2) \cdot \exp\{i\,\vartheta\,I_y\}$ between the nuclear quadrupole moment $e\,Q$ and the electric field gradient $e\,q$.

The pure magnetic interaction produces an equidistant splitting of the five levels (Figure 3 a). This equidistance is removed by the additional quadrupole interaction, which depends on the orientation of the crystal. Since the angle $\vartheta$ is the same for all $^{20}$F nuclei, one expects one single quadrupole splitted spectrum consisting of four lines.

## 3. Experimental

### 3.1. *Crystal Growth*

KZnF$_3$ single crystals were grown by the Bridgman technique. The starting material was polycrystalline KZnF$_3$ (impurity level $<100$ ppm), prepared by melt reaction of stoichiometric mixtures of reagent grade KF, which had been purified by crystal growth, and reagent grade ZnF$_2$, which had been purified by vacuum sublimation. Crystal growth was performed in a high vacuum crystal growing furnace as constructed by us for this special purpose. The self supporting heater is a bifilar graphite helix. To reduce evaporation of KZnF$_3$ closed graphite crucibles were used. To remove oxygen the chamber was evacuated and then filled with Argon (pressure 0.4 atm). Growth conditions were: temperature of the melt ca. 900 °C (melting point of KZnF$_3$ 860 °C), vertical temperature gradient in the furnace 40 degrees cm$^{-1}$, growth velocity 0.24 cm h$^{-1}$. Single crystals grown from stoichiometric melts (KF : ZnF$_2$ = 1 : 1) were hygroscopic and of poor transparency because of KF inclusions. This disadvantage was avoided successfully by adding 2 weight-% ZnF$_2$ to the initial stoichiometric KZnF$_3$ charge. The asgrown crystals were perfectly transparent. The size of the crystals was determined by the dimensions of the crucibles (diameter 15 mm, length up to 40 mm).

### 3.2. *Apparatus*

The experimental technique was similar to that described in a preceding experiment on MgF$_2$ [5]. A thermal neutron beam of the guide H25 at the High Flux Reactor Grenoble was spin polarized by reflection from a magnetized Co$_{50}$Fe$_{50}$ mirror, yielding about $5 \cdot 10^7$ cm$^{-2}$ s$^{-1}$ polarized neutrons at the target (Figure 2). The KZnF$_3$ target (two pieces each $20 \times 25 \times 2$ mm$^3$) was placed in an external magnetic induction $B_0 = 0.5$ T. As already mentioned, the crystal was oriented with the [111]-axis parallel to $B_0$ with an accuracy of $\pm 1.5°$. The radio-frequency (rf) coil for the induction of NMR transitions consisted of eight windings of aluminium wire ($\phi$ 0.4 mm) around the crystal. The polarization of the activated $^{20}$F nuclei was detected via their asymmetric $\beta$-decay. The $\beta$-radiation was registered by two scintillator telescopes mounted on both sides of the target in the pole gap. The $\beta$-particle counting rates in each of the two telescopes were about 100 s$^{-1}$ and the typical measuring time for one asymmetry value was 2 h. The measurements were performed at room temperature.

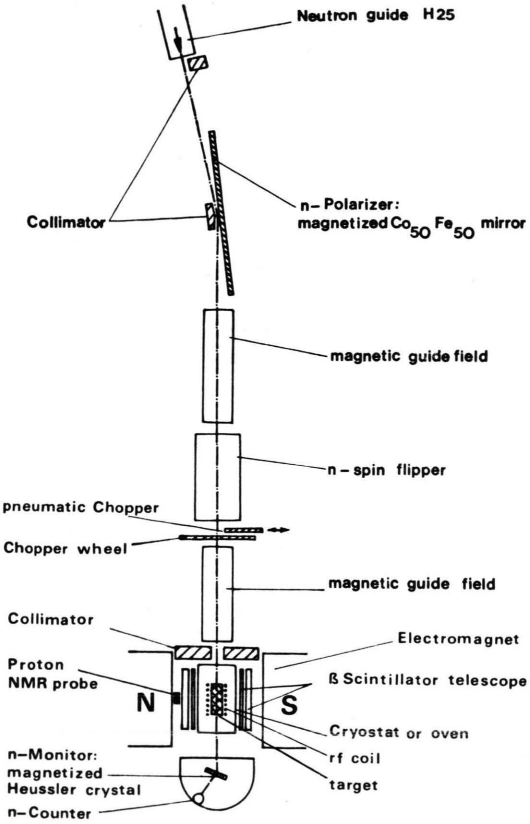

Fig. 2. Experimental set-up.

## 4. Measurements and Results

For the determination of the quadrupole coupling constant $e^2 q Q$ we applied a procedure described elsewhere in greater detail [5]. At first a broad modulated rf-band was shifted over the frequency range of interest to determine the approximate position of the four $\Delta m = \pm 1$ transitions. To improve the accuracy, we studied also a single transition at 3 MHz. To this end one rf-field $\nu_1$ was varied step by step over the NMR-transition. The radio frequency was modulated by ± 100 kHz in order to account for possible inhomogeneous line broadening (caused e. g. by inhomogenities of $B_0$, by different orientation of the two target crystals, or by interaction of the $^{20}$F nuclei with neighbouring defects). Simultaneously a second broad-band modulated rf-field $\nu_2$ saturated the other rf-transitions. The effect of the second rf-field is to increase considerably the resonance depth of the single transition. The resonance curve, obtained in this way, is shown in Figure 3 b. From the four resonance frequencies the quadrupole coupling constant of $^{20}$F in KZnF$_3$ could be determined with the result

$$|e^2 q Q/h| = (12.0 \pm 1.5)\ \text{MHz}.$$

The comparatively large error stems from the ± 100 kHz modulation of the rf-field $\nu_1$.

For an independent check we also measured the dependence of the $\beta$-decay asymmetry on the magnetic induction $B_0$, see Figure 4. At low values of $B_0$ the nuclear polarization is attenuated by the electric quadrupole interaction. By a high $B_0$ the quadrupole interaction can be decoupled and the initial polarization is restored. The full line in Fig. 4 is the theoretical curve calculated for $|e^2 q Q/h| = 12$ MHz with help of the formulae in Reference [8]. The sign of the quadrupole interaction was obtained from the measurement of a small $\gamma$-ray anisotropy in the $\gamma$-transition in $^{20}$Ne* following the $^{20}$F-decay; for details of the method see Reference [9]. We found an anisotropy: $a_\gamma = +(0.054 \pm 0.036)$ % when the two transitions with the upmost frequencies were saturated and no anisotropy: $a_\gamma = -(0.016 \pm 0.034)$ when no rf was induced. From this we conclude that $e^2 q Q$ is positive, with a confidence level of 93%.

With the known quadrupole moments $|Q(^{20}\text{F})| = 0.064(12)$ b and the theoretically predicted [10] positive sign of $Q(^{20}\text{F})$ we obtain for the electric field gradient

$$e\,q = +(7.7 \pm 1.7)\ 10^{17}\ \text{Vcm}^{-2}.$$

This value agrees with an unpublished result [11] for $|e\,q|$ obtained with the above mentioned method of perturbed angular correlations using the excited 197 keV-state of $^{19}$F. Contrary to these measurements, which do not consider any crystal orientation (and work as well in powders) our measurement on a single crystal gives also the main axis of the electric field gradient tensor. This makes it easier to rule out field gradients from eventual static lattice defects. We conclude that in the case of KZnF$_3$ the radioactive nuclei produced by the (p, p′ $\gamma$)- or the (n, $\gamma$)-process come to rest at normal lattice sites and the produced defects anneal so quickly at room temperature that they do not disturb the observed spectra.

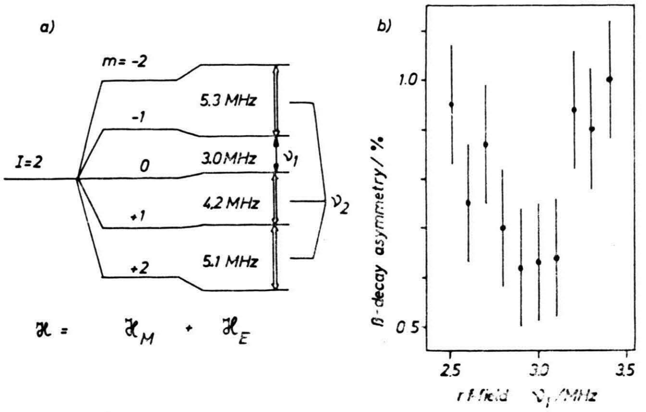

Fig. 3. a) Splitting of the ground state of $^{20}$F for a pure magnetic interaction and for both magnetic and electric interactions. The magnetic induction was $B_0 = 0.5\ T$, the crystal was oriented with the [111]-axis parallel to $B_0$. b) Single rf-transition. The rf-field $\nu_1$ was modulated by ±100 kHz. Simultaneously the three rf-transitions were saturated by a second broad band modulated rf-field $\nu_2$.

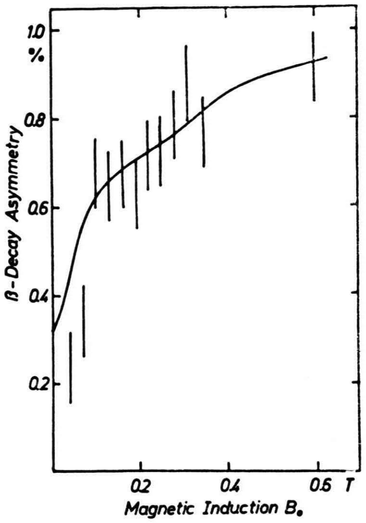

Fig. 4. Experimental and theoretical dependence of the $\beta$-decay asymmetry on the magnetic induction $B_0$. The crystallographic [100]-axis was oriented along $B_0$.

## 5. Discussion

The experimental results will now be discussed following the lines of Bersohn and Shulman[12] who considered quadrupole coupling constants in terms of antibonding molecular orbitals. s-p hybridisation is neglected, because in weakly covalent transition metal complexes the degree of s electron bonding has been shown to be negligible[13, 14]. Townes and Dailey[15] assumed that the contribution of the p electrons to the quadrupolar interaction dominates. Therefore it can be shown[12] that the excess hole density in the ligand *p* orbital along the direction of the maximum field gradient, $f_Q$, is

$$f_Q = \frac{(e^2\,q\,Q/h)_{\text{crystal}}}{(e^2\,q\,Q/h)_{\text{atom}}\,n_h} = \frac{q_{\text{crystal}}}{q_{\text{atom}}\,n_h},$$

where $n_h$ is the number of holes in a certain metal orbital prior to bonding. $f_Q$ measures the difference in total electron density between $\sigma$ and $\pi$ orbitals. Therefore the $f_Q$ values change in the same manner as the $f_\sigma - f_\pi$ values, obtained from ESR spectra, if a simple covalent picture including only d-p type effects is utilized. These changes indicate corresponding decreases or increases in covalency of the metal-halogen bond.

For the calculation of the $f_Q$ values the field gradient and the quadrupole moment or the quadrupole coupling constant of the free atom must be known. To this purpose the field gradient of the free fluorine atom which does not depend on the isotope considered is determined[16] by an ab initio calculation including configuration interaction

$$e\,q = 8.3 \times 10^{18}\ \text{Vcm}^{-2}$$

yielding an $f_Q$ value of 4.6% for KZnF$_3$.

This value is compared with the corresponding $f_Q$ data of some KMF$_3$ and CsMCl$_3$ compounds shown in Table 1. The trend in the $f_Q$ is best explained, if a constant ionic contribution to the field gradient is subtracted[3]. The decrease of the $f_Q$ values of the chlorine containing compounds indicates a pro-

Table 1. $f_Q$ values of the compounds CsMCl$_3$ and KMF$_3$.

| Compound | $f_Q$ | $f_{Q\ \text{recalc.}}$ and this work |
|---|---|---|
| CsMnCl$_3$ | 7.4; 8.2 [a] | |
| CsCoCl$_3$ | 8.4 [a] | |
| CsNiCl$_3$ | 15.1 [b] | |
| CsCuCl$_3$ | 19.3; 20.3 [b] | |
| CsMgCl$_3$ | 6.4 [a] | |
| KMnF$_3$ | 4.8 [c] | 2.6 [e] |
| KCoF$_3$ | 7.3 [c] | 3.9 [e] |
| KNiF$_3$ | 8.9 [c] | 4.8 [e] |
| KZnF$_3$ | | 4.6 [d] |

[a] Ref.[17]. [b] Ref.[18]. [c] Ref.[3]. [d] This work.

[e] Recalculated values using the free atom field gradient value for fluorine $eq = 8.3 \cdot 10^{18}\ \text{Vcm}^{-2}$ given in this paper

nounced increase of covalency in the order:

$$CsMnCl_3 < CsCoCl_3 < CsNiCl_3 < CsCuCl_3$$

parallel to the position of the transition metal in the periodic table.

The $f_Q$ values of the three fluorides $KMnF_3$, $KNiF_3$, and $KCoF_3$ have been determined by Haas et al.[3] in a $\gamma$-ray perturbed angular distribution experiment in the $5/2^+$ state of $^{19}$F. The authors used $(e^2 q Q/h)_{\text{atom}} = 120$ MHz estimated from measurements with $^{19}F(5/2^+)$ in ClF and $(C_2F_4)_n$[1]. However, utilizing the known quadrupole moment of this excited fluorine state, $Q(^{19}F, 5/2^+) = 0.11$ b[1], and our calculated field gradient in the free atom, we obtain a much higher value: $(e^2 q Q/h)_{\text{atom}} = 222$ MHz. The $f_Q$ values of the three compounds considered above, recalculated with this coupling constant are the $f_{Q,\text{recalc.}}$ figures in Table 1.

The recalculated $f_Q$ values of $KMnF_3$, $KNiF_3$, and $KCoF_3$ and our $f_Q$ of $KZnF_3$ are smaller than the corresponding values of the chlorine containing compounds. The order of the covalency change is now:

$$KMnF_3 < KCoF_3 < KNiF_3 \cong KZnF_3 .$$

It is surprising that the $f_Q$ values of $KNiF_3$ and $KZnF_3$ are about equal whereas the values of $CsNiCl_3$ and $CsCuCl_3$ differ by 25%, although Zn and Cu are in adjacent groups of the periodic table. The discrepancy may be caused by differences in the crystal structures between the chlorides and the fluorides (all the fluorides have the cubic perewskite structure). However, it seems to be more to the point to consider the different properties of chemical bondings containing chlorine or fluorine. Furthermore, it must be taken into account, that the $Zn^{+2}$ ion is the only one of the metal ions discussed with a $d^{10}$ configuration.

## *Acknowledgement*

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