The Nuclear Magnetic Shielding of the $^{19}$F-Nuclei in KZnF$_3$

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Z. Naturforsch. 40a, 283–293 (1985); received December 20, 1984

Using solid state multiple pulse techniques the magnetic shielding tensors $\sigma$ of the $^{19}$F nuclei in a single crystal of KZnF$_3$ have been measured. The F$^-$-site symmetry in KZnF$_3$, $D_{4h}$, allows axial anisotropy of $\sigma$ and determines fully the principal shielding directions. Using CaF$_2$ as the reference compound, the average shielding is $+85$ ppm and the shielding anisotropy is $+18.4$ ppm. These results are discussed in terms of shielding contributions from (a) the closed shell electrons of the F$^-$-ion whose shielding is considered, (b) the closed shell electrons of the neighbouring metal and fluorine ions and (c) weak admixture of covalency to the predominantly ionic Zn$^{++}$–F$^-$ bonding.

1. Introduction

The development of multiple pulse techniques [1, 2] has made possible the measurement of nuclear magnetic shielding tensors of $^{19}$F nuclei in the solid state. The $^{19}$F shielding has been studied in the past in a variety of compounds with either dominant ionic or covalent bonding, and the results have been discussed in terms of the bonding [3].

In this communication we report on measurements of the shielding tensors of the fluorines in KZnF$_3$. Crystals of this compound are thought to be strongly ionic. We expected and indeed found that the $^{19}$F-$\sigma$ tensors reflect the dominant ionic character of the bonding, but at the same time it is interesting to investigate to what extent the admixture of weak covalency affects the $^{19}$F magnetic shielding. A major part of the discussion of our results is concerned with this question.

In most of the fluorides studied so far the shielding is isotropic as a result of cubic fluorine site symmetry [3]. In KZnF$_3$ the F$^-$-site symmetry permits an axially symmetric shielding anisotropy. Other cases where symmetry permits shielding anisotropy are MgF$_2$, ZnF$_2$ and SnF$_2$. The $^{19}$F shielding tensors reported for these compounds [4, 5] are, therefore, best suited for comparison purposes with our results from KZnF$_3$.

By using the radioactive $^{20}$F nucleus ($I = 2$) Ackermann et al. [6] have recently measured the electric field gradient (EFG) tensor at the fluorine site in KZnF$_3$. We discuss the question whether and how the nuclear magnetic shielding tensor $\sigma$, which can be measured by comparatively simple RF-techniques, can be related to the EFG tensor whose measurement requires techniques and equipment from the arsenal of the nuclear physicist.

2. Symmetry Considerations

KZnF$_3$ has a perowskite-like structure [7]. Figure 1 shows the arrangement of the ions in the unit cell. Each fluorine sits on a fourfold axis which is colinear to the Zn–F–Zn bonds. The local symmetry at the F$^-$-site is $D_{4h}$. This symmetry imposes axial symmetry on the $^{19}$F-$\sigma$-tensor. Its unique direction must be along the Zn–F–Zn direction, i.e., along one of the primitive crystal axes. There are three symmetry related fluorine ions in the unit cell.

Fig. 1. Packing of the ions in the unit cell of KZnF$_3$. Open spheres: F$^-$; full spheres: Zn$^{++}$, speckled sphere: K$^+$. 

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cell. As a consequence of this crystal symmetry complete information about the $^{19}$F-shielding symmetry tensor $\mathbf{\sigma}$ can be obtained from a single spectrum taken with $B_0$ parallel to one of the crystal axes, e.g., $B_0 \parallel 100$. For such a crystal orientation $B_0$ is parallel to the Zn–F–Zn direction of one, and perpendicular to the Zn–F–Zn directions of the other two of the three F$^-$-ions in the unit cell, see Figure 1. For this orientation we expect, hence, two NMR lines with an intensity ratio of 1:2. The smaller of the lines reflects $\sigma_\perp$, the larger $\sigma_\parallel$, their separation gives directly the shielding anisotropy $\Delta \sigma = \sigma_\parallel - \sigma_\perp$.

According to these considerations we prepared a sample crystal such that its $c$-axis was parallel to the NMR goniometer axis which itself is perpendicular to $B_0$. This allows to align the $a$- as well as the $b$-axis of the crystal parallel to $B_0$.

For a general orientation of the crystal relative to $B_0$ we expect three NMR lines. All these lines must coincide for $B_0 \parallel (111)$.

3. Experimental and Results

The $^{19}$F high resolution NMR measurements were performed on a 90 MHz Bruker pulse spectrometer modified for multiple pulse experiments. The spectra were obtained with a phase error and flip-angle error self correcting version of the MREV cycle [2]. The width of the $\pi/2$ pulses was 0.8 $\mu$sec, their separation 3 $\mu$sec and 6 $\mu$sec, respectively. This method averages out the $^{19}$F–$^{19}$F homonuclear part of the dipole-dipole Hamiltonian. The heteronuclear dipole interactions, $^{19}$F–$^{67}$Zn and $^{19}$F–$^{39}$,$^{41}$K, are only scaled down by a factor of $\sqrt{2}/3$. The shortest inter-nuclear distances, and hence potentially the strongest DD interactions, are between the $^{19}$F and Zn nuclei. Fortunately, the natural abundance of the magnetic Zn isotope $^{67}$Zn is only 4.12% so that most of the $^{19}$F nuclei have non-magnetic Zn isotopes as their nearest neighbours. The other non-averaged dipolar interaction, between K and F nuclei, is weak since the shortest K–F distance in KZnF$_3$ is rather large ($a/\sqrt{2}$ with $a = 4.055 \AA$) and the gyromagnetic ratios of both the $^{39}$K and $^{41}$K isotopes are small. These interactions, nevertheless, limit the resolution in our spectra. A second moment calculation of the K–F interactions accounts well for the observed linewidths.

A spectrum for $B_0 \parallel (100)$ is shown in Figure 2. It shows indeed two lines with the expected intensity ratio of 2:1. The separation of the lines is 18.4 ppm and corresponds, as mentioned above, directly to $\Delta \sigma$. Further spectra were recorded for different orientations of $B_0$ in the $a-b$ plane. The analysis of the rotation pattern of the line shifts helped to minimize errors in our final numbers which resulted from a small misorientation of the sample crystal. A sphere of a single crystal of CaF$_2$ was used as the reference compound.

The chemical shift tensor of the $^{19}$F nuclei in KZnF$_3$ derived from our data is given in Table 1. In order to compare our results with theoretical calculations the principal values of $\mathbf{\sigma}$ must be given on an absolute scale. For $^{19}$F such a scale was established by Hindermann et al. [8]. The second line of Table 1 gives $\mathbf{\sigma}$ in KZnF$_3$ on this scale.

![Fig. 2. Multiple pulse spectrum of a single crystal of KZnF$_3$; $B_0$ parallel (100).](image)

### Table 1. $^{19}$F shielding tensor in KZnF$_3$ (all units in ppm).

<table>
<thead>
<tr>
<th></th>
<th>$\sigma$</th>
<th>$\sigma_\parallel$</th>
<th>$\Delta \sigma$</th>
<th>$\sigma_\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong> reference: CaF$_2$</td>
<td>97.4</td>
<td>78.8</td>
<td>18.6</td>
<td>85</td>
</tr>
<tr>
<td><strong>Experimental absolute scale</strong></td>
<td>390</td>
<td>371.4</td>
<td>18.6</td>
<td>377.6</td>
</tr>
</tbody>
</table>

**Contributions**

1. closed shell F$^-$-ion
2. geometrical
3. departure from pure ionic model
4. diamag. (overlap and covalency)
5. paramagnetic (overlap and covalency)

- a Absolute scale according to [8].
- b Calculated using Pascal's constants.
- c Obtained by subtracting contributions 1 and 2 from the experimental values on the absolute scale.
4. Discussion

The main features of our experimental results may be summarized as follows:

- the unique axis of the axially symmetric $^{19}$F-σ-tensor corresponds to the most shielded direction and is along the “bonding” direction Zn–F–Zn.
- the anisotropy of σ is small compared with the size of the individual components of σ taken on the absolute scale.

The feature of the $^{19}$F-σ-tensor which reflects most directly the ionic nature of the bonding in KZnF$_3$ is the small size of ∆σ. This can be seen by analysing the different contributions to σ, see further below, but also on a simple comparative basis. Other fluorides whose $^{19}$F shielding has been investigated by high resolution solid state NMR and where crystal symmetry does not prohibit shielding anisotropies are MgF$_2$, ZnF$_2$ and SnF$_2$. In neither of these compounds crystal symmetry forces σ to be axially symmetric. MgF$_2$ and ZnF$_2$ are typical ionic compounds, the differences between the largest and the smallest $^{19}$F principal shielding components are 30 ppm (MgF$_2$) and 44 ppm (ZnF$_2$), see [4]. SnF$_2$, on the other hand, forms rings of tetramers, Sn$_4$F$_8$, with four different fluorine sites. The shielding anisotropies, ∆σ = 210, 165, 106 and 97 ppm (sites 1–4) are comparable in size to the shielding anisotropies of typically covalently bound fluorides, see Table 5.4 of [1]. Along with other evidence the “large” shielding anisotropies measured in SnF$_2$ have, consequently, been interpreted as signalizing predominantly covalent bonding of the SnF$_4$ tetramers. The shielding anisotropy, and, of course, plenty other chemical and physical evidence as well, puts KZnF$_3$ in one class with MgF$_2$ and ZnF$_2$, i.e., in the class of predominantly ionic fluorides.

We proceed by analysing the origin of different contributions to σ in KZnF$_3$.

According to the general theory of the chemical shift [9], σ can be split into a dia- and into a paramagnetic term:

$$\sigma = \sigma^d + \sigma^p,$$

(1)

where

$$\sigma^d_{ij} = \frac{e^2}{2m c^2} \sum_k \frac{r_k^2 \delta_{ij} - r_{ki} \cdot r_{kj}}{r_k^3} \langle \psi_0 | \psi_m \rangle$$

(2)

and

$$\sigma^p_{ij} = \frac{e^2}{2m c^2} \sum_m \left( E_0 - E_m \right)^{-1}$$

$$\cdot \left\{ \langle \psi_0 | \sum_k l_{ki} / r_k^2 | \psi_m \rangle \langle \psi_m | \sum_k l_{kj} / r_k^2 | \psi_0 \rangle \right. +$$

$$\left. \langle \psi_0 | \sum_k l_{ki} / r_k^2 | \psi_m \rangle \langle \psi_m | \sum_k l_{kj} | \psi_0 \rangle \right\}.$$
where the $P_{\beta}^{A}\beta = \sum_{j} 2 A_{j}(j) A_{\beta}^{A}(j)$ are the matrix elements of the charge density matrix $P$ [10].

If the $A_{j}(j)$ are real then $P_{\beta}^{A}\beta = P_{\beta}^{A}\beta$. Before discussing different possibilities of constructing MOs for KZnF$_3$ we consider the order of magnitude of different terms in (7)–(8), disregarding the size of $P_{\beta}^{A}\beta$.

Label the nucleus of interest as $l = 0$, then:

- $\langle \phi_{l}^{A} | l_{x} | \phi_{l}^{A} \rangle$ either zero or of the order of $\langle \phi_{l}^{A} | \phi_{l}^{A} \rangle = 1$.
- $\langle \phi_{l}^{A} | r_{x}^{2} | \phi_{l}^{A} \rangle$ and $\langle \phi_{l}^{A} | l_{x} | \phi_{l}^{A} \rangle$ are either zero or of the order of $\langle 1/r \rangle_0$ and $\langle 1/r^3 \rangle_0$, respectively.
- $\langle \phi_{l}^{A} | l_{x} | \phi_{l}^{A} \rangle$ is of the order of $\langle \phi_{l}^{A} | 1/r^3 \rangle_{l}$.

This again is a two-center integral but much smaller than $\langle 1/r^3 \rangle_0$.

All other terms are either three-center integrals or products of two-center integrals.

Therefore the main contributions in (7) and (8) are expected to come from terms proportional to $\langle 1/r \rangle_0$, $\langle 1/r^3 \rangle_0$ or $\langle \phi_{l}^{A} | 1/r | \phi_{l}^{A} \rangle$ and from those which contain products of the form $\langle 1/r^3 \rangle_0$ $S_{l}^{A}\beta$. Since the local symmetry of the F$^{19}$-nucleus in KZnF$_3$ is $D_{4h}$, we are interested only in $\sigma_{xx}$ and $\sigma_{zz}$. As the nucleus of interest ($l = 0$) is F$^{19}$ we shall take as basis for $\phi_{l}^{A}$ the set $2s$, $2p_{x}$, $2p_{y}$, $2p_{z}$. Retaining only the contributions linear in $\langle 1/r \rangle_0$, $\langle 1/r^3 \rangle_0$ and $\langle \phi_{l}^{A} | 1/r | \phi_{l}^{A} \rangle$, (7) and (8) can be brought into the following form:

$$\sigma_{xx}^{l} = \frac{e^2}{2m c^2} \sum_{l} P_{l}^{A}\beta \langle \phi_{l}^{A} | \frac{r^2 - x^2}{r^3} | \phi_{l}^{A} \rangle,$$

$$\sigma_{zz}^{l} = \frac{e^2}{2m c^2} \sum_{l} P_{l}^{A}\beta \langle \phi_{l}^{A} | \frac{r^2 - z^2}{r^3} | \phi_{l}^{A} \rangle,$$

and

$$\sigma_{xx}^{p} = - \frac{e^2 h^2}{\Delta m^2 c^2} \langle 1/r^3 \rangle_0 \left\{ \left[ P_{l0}^{a}P_{l0}^{b} - (P_{l0}^{a}P_{l0}^{a} - P_{l0}^{a}P_{l0}^{a}) \right] ight.$$

$$- \sum_{l} \left[ (P_{l0}^{a}P_{l0}^{a} - P_{l0}^{a}P_{l0}^{a}) S_{l0}^{a} ight.$$  

$$+ (P_{l0}^{a}P_{l0}^{a} - P_{l0}^{a}P_{l0}^{a}) S_{l0}^{a} \bigg]$$

$$\sum_{l} \sum_{x,\beta} P_{l0}^{a}\beta \langle \phi_{l0}^{A} | l_{x} | \phi_{l0}^{A} \rangle \left| m/h \right| \bigg],$$

$$\sigma_{zz}^{p} = \sigma_{zz}^{p} = 0.$$

The calculation of $P_{l0}^{a}\beta$ requires the knowledge of $\psi_{l}$. The MOs $\psi_{l}$ may be constructed by different methods. Since KZnF$_3$ is mainly ionic we shall consider the following approximations:

A) The wavefunctions $\psi_{l}$ are purely ionic. In this approximation the non-orthogonality of MOs on different nuclei is disregarded.

B) The MOs are obtained by Löwdin's orthogonalization method [11]. The $\psi_{l}$ are still mainly ionic but orthogonal.

C) Covalent bonding between F$^{-}$ and Zn$^{2+}$ electrons is taken into account. We shall discuss approximations A to C in turn.

A) If $\psi_{l}$ is purely ionic $\psi_{l} = \phi_{l}^{A}$ and $P_{l0}^{a}\beta = 2$, $P_{l0}^{a}\beta = 0$.

Equations (10)–(13) become

$$\sigma_{xx}^{l} = \frac{e^2}{2m c^2} \left[ \sum_{l} \langle \phi_{l}^{A} | \frac{r^2 - x^2}{r^3} | \phi_{l}^{A} \rangle \right.$$  

$$+ \sum_{l} \langle \phi_{l}^{A} | \frac{r^2 - x^2}{r^3} | \phi_{l}^{A} \rangle \bigg],$$

$$\sigma_{zz}^{l} = \frac{e^2}{2m c^2} \left[ \sum_{l} \langle \phi_{l}^{A} | \frac{r^2 - z^2}{r^3} | \phi_{l}^{A} \rangle \right.$$  

$$+ \sum_{l} \langle \phi_{l}^{A} | \frac{r^2 - z^2}{r^3} | \phi_{l}^{A} \rangle \bigg],$$

and $\sigma_{xx}^{p} = \sigma_{zz}^{p} = 0$.

The first terms in (14) and (15) are the ionic contributions due to the closed shells of electrons on the F$^{-}$-ion under investigation. For these terms we rely on work of Sidwell and Hurst [12] who obtained $\sigma_{xx}^{p}$ (free ion) = $\sigma_{zz}^{p}$ (free ion) = 480 ppm.
The second terms in (14) and (15) are the contributions from the closed shells of neighbouring ions. These contributions, sometimes called "geometrical" can be calculated by inserting appropriate wave functions in (14)–(15) and integration. This procedure was used in [4] for MgF$_2$. To take account of these contributions, we shall use the phenomenological magnetic dipole model [13]. In this model induced magnetic dipoles are assigned to individual ions. The fields associated with these dipoles give the following contribution to the shielding of the nucleus of interest:

$$
\sigma(g) = \sigma^d(g) = 1/L \sum_k \left( \chi^k/R_k^3 - 3(\chi^k R_k) R/R^5 \right). \tag{16}
$$

g means "geometrical", $L$ is Loschmidt's number, $\chi^k$ the molar susceptibility of the $k$-th ion. For the evaluation of $\sigma(g)$ we used for the susceptibilities Pascal's constants [14]. The summation was extended over 50 neighbours. The results are given in line 4 of Table 1.

Note that the values of $\sigma^d(g)$ and $\sigma^d_0$ are small compared with the experimental ones on the absolute scale and as well small compared with $\sigma$ (free ion). Note also that the anisotropy $\Delta \sigma^d(g)$ is comparable in size with $\Delta \sigma$ (exptl.).

In order to check the reliability of the dipole model we calculated $\sigma^d(g)$ for MgF$_2$ using (16) and compared the results with those of [4] obtained by integration. The two methods give results which differ by no more than 1–2 ppm. We do not consider differences of this size as essential.

$\sigma^d$ (free ion) and $\sigma^d(g)$ appear unchanged in the approximation of MOs to be discussed now and therefore will not be considered anymore.

The values reported in the fifth line of Table 1 are obtained by subtracting $\sigma^d$ (free ion) and $\sigma^d(g)$ from the experimental values. They reflect the contributions brought in by the departure of the wave functions from their purely ionic form and will be referred to henceforth as "non-ionic contributions".

B) Löwdin's orthogonalization method [11] provides the following set of wave functions

$$
\psi_j = \psi^f_j = \phi^f_j - \frac{1}{2} \sum_{k \beta} S^f_{kj} \phi^f_{k \beta} + \frac{3}{8} \sum_{k \beta n \gamma} S^f_{k \beta n} S^f_{n \gamma} \phi^f_{k \beta} + \ldots \tag{17}
$$

which leads to

$$
\begin{align*}
P^{00} &= 2 \left[ 1 + \sum_{k \gamma} (S^f_{k \gamma})^2 \right], \\
P^{0\beta} &= 2 \sum_{k \gamma} S^f_{k \gamma}^2 \phi^f_{k \beta}, \\
P^{\beta\beta} &= -2 \sum_{k \gamma} \left[ S^f_{k \gamma} - \frac{3}{2} S^f_{k \gamma}^2 \right]. \tag{18}
\end{align*}
$$

using (18) and (10)–(13) one obtains

$$
\begin{align*}
\sigma^d_{x,x} &= -\frac{2e^2}{5mc^2} \langle 1/r \rangle_{F_{2x}} \\
&\cdot \sum_{ls} [ S^0_{ls}^y + S^0_{ls}^z + \frac{1}{2} S^0_{ls}^z ] , \\
\tag{20}
\end{align*}
$$

and corresponding expressions for $\sigma^d_{y,y}$ and $\sigma^d_{z,z}$.

In (17)–(21) all terms containing overlap integrals of power higher than two were neglected. The contributions of different neighbours are additive. It should be noted that the same result is obtained if one uses a simpler set of wave functions which ensures only the orthogonality of wave functions on neighbouring ions with those on the ion of interest ($l = 0$):

$$
\begin{align*}
\psi^0_j = \phi^0_j , \\
\psi^f_j = \left[ \phi^f_j - \sum_{\beta} S^0_{j \beta} \phi^f_{\beta} \right]/\left[ 1 - \sum_{\beta} (S^0_{j \beta})^2 \right]^{1/2} . \tag{22}
\end{align*}
$$

The equivalence appears immediately if one observes that within the same approximations (22) leads to

$$
\begin{align*}
P^{00} &= 2 \left[ 1 + \sum_{ls} S^0_{ls}^2 \right] , \quad \text{etc.}
\end{align*}
$$

The set of wave functions given by (17) and their consequence, (20) and (21) have been widely used in chemical shift calculations in many predominantly ionic crystals [4, 15, 16]. Nevertheless, (17) or its simplified form, (22) excludes any covalent effects which in the case of metal-halogen (Zn-F) bonding may be of the same order of magnitude as the overlap contributions as far as the anisotropy $\Delta \sigma$ is concerned. Therefore, detailed evaluations of 20 and 21 will be given once the covalency effect is taken into account. In fact, our calculations (see further below) have shown that (20) leads to negligibly small contributions to $\Delta \sigma^d$ and $\sigma^d$ as expected [15, 16]. On the
other hand, (21) leads to a calculated value of the ratio $\Delta \sigma^p/\sigma^p$ which is almost one order of magnitude smaller than that obtained with the semiexperimental numbers from line 5 of Table 1, and the sign is opposite. Therefore we looked for possible effects of weak covalent bonding between Zn$^{++}$ and F$^-$. 

C) Covalency may make an important input to the chemical shift tensor since it leads to a strong delocalization of electrons and therefore to a more important departure of the wave functions from their ionic form than that predicted by (17).

In the case of KXF$_3$ crystals it was shown [17] that covalency arises mainly from the interactions between (2s, 2p)-electrons of the F$^-$ and 3d-electrons of the X$^{++}$-ions, leading to bonding and antibonding states. We consider only the interactions between F$^-$ (0, 0, 0) and its two Zn-neighbours at (0, 0, $\pm \frac{1}{2}$). The bonding (b) and antibonding (a) MOs which transform according to irreducible representations of D$_{4h}$ (F$^-$-site symmetry) are:

$$\psi^b_r (e_u) = \frac{1}{\sqrt{N^b(e_u)}} \left[ p_r + b_r \gamma_r \right], \quad (r = x, y)$$

(23)

$$\psi^a_r (e_u) = \frac{1}{\sqrt{N^a(e_u)}} \left[ \gamma_r - a_r p_r \right], \quad (r = x, y)$$

(24)

with

$$\gamma_r (e_u) = \frac{1}{\sqrt{2}} \left[ d_{1z} (\frac{1}{2}) + d_{2z} (\frac{1}{2}) \right],$$

$$\gamma_z (a_{2u}) = \frac{1}{\sqrt{2}} \left[ d_{1z} (\frac{1}{2}) - d_{2z} (\frac{1}{2}) \right].$$

(25)

The normalization factors are:

$$N^b_2 = 1 + b_2^2 + 2 b_u S_2, \quad N^a_2 = 1 + a_2^2 - 2 a_z S_2,$$

with $a_2 = (b_2 + S_2)/(1 + b_2 S_2)$ and $S_2 = \langle p_z | \gamma_z \rangle$.

The wave functions of electrons on neighbour ions, K$^+$ and F$^-$, which do not participate in the bonding are taken of the form (22) in order to ensure orthogonality. This set of wave functions leads to the following result:

$$\sigma^p_{xx} = \sigma^p_{xx} (N) + \sigma^p_{xx} (Zn),$$

$$\sigma^p_{zz} = \sigma^p_{zz} (N) + \sigma^p_{zz} (Zn).$$

(26)

$\sigma^p_{xx} (N)$ and $\sigma^p_{zz} (N)$ are given by (21) and reflect the overlap contributions of K$^+$ and F$^-$-neighbours. The second terms in (26) are:

$$\sigma^p_{xx} (Zn) = -\frac{4 e^2 \hbar^2}{\Delta m^2 e^2} \langle 1/r^3 \rangle_{F2p}$$

$$\cdot \left[ S_{10}^{zz} \right]^2 + S_{10}^{zz} \right] - 2 \sqrt{3} S_{10}^{zz} S_{10}^{yy} \right],$$

(27)

$$\sigma^p_{zz} (Zn) = -\frac{4 e^2 \hbar^2}{\Delta m^2 e^2} \langle 1/r^3 \rangle_{F2p}$$

$$\cdot \left[ S_{10}^{zz} \right]^2 + S_{10}^{zz} \right] - 2 S_{10}^{zz} S_{10}^{yy} \right].$$

$S_{10}^{\alpha}$ stands for the overlap integral between the d$_{z^2}$ wave function of Zn$^{++}$ at (0, 0, $\pm \frac{1}{2}$) and the p$_\alpha$-wave function of F$^-$ at (0, 0, 0).

This result is easily obtained if one observes that the set of wave functions (22) and (23)–(25) gives

$$P_{l0}^{zz} = 2 \left[ 1/N_2^l + a_2/N_2^l + \sum_{k\beta} S_{l0}^{\beta} S_{l0}^{\alpha} \right]$$

(27)

$(k$ runs over the K$^+$, F$^-$-neighbours),

$$P_{l0}^{zz} = 2 \left[ b_2/\sqrt{2 N_2^l} - a_2/\sqrt{2 N_2^l} \right] \quad \text{for } l = 1, 2 \ (Zn^{++})$$

and

$$P_{l0}^{zz} = -2 S_{l0}^{zz} \quad \text{for } l = 1, 2 \ (Zn^{++})$$

which, when inserted into (8), give (26) and (27).

In fact, the result of (27) is also contained in (20) and (21). The summations in the latter equations include the Zn$^{++}$-neighbours and it can be easily shown that their contributions are identical to (27). It shows that for weak covalent bonding, as long as one considers fully occupied bonding and antibonding states, the final result depends only on overlaps between neighbours and is entirely equivalent to that obtained with Löwdin's set of wave functions (at least within the present approximations).

It should be noted that the MOs given in (23) to (24) imply a (slight) delocalization of the electrons on the F$^-$-ion which results entirely from mixing of F$^-$-AOs and Zn$^{++}$-AOs. That this is the dominant delocalization is questionable since many results obtained by N.M.R., E.P.R. and optical methods in KXF$_3$-crystals (X = Mn, Ni) could be explained by weak covalent bonding between the central ion (X) and its six next fluorine neighbour ions whose electrons were assumed to occupy ligand orbitals (17). Ligand orbitals imply a stronger delocalization than that given by (23). In fact, in these works the covalency effects were investigated within the fragment XF$_6$ (O$_h$-symmetry). Therefore we considered it interesting to evaluate the chemical shift of F$^{19}$ in...
this fragment \(\text{(X = Zn)}\) using the same type of wave functions as in the above mentioned works and to compare the results with those obtained with the previous sets of wave functions as given by (17) and (23) - (25). The calculations carried out in the Appendix give a result which is equivalent to (26) and (27) as long as the bonding and antibonding states are fully occupied. The main advantage of considering \(F^+-\text{ligand}\) orbitals is that one may easily envisage the effects of non-occupied antibonding states. We shall turn to this point now, discussing it for the \(XF_6\) fragment. An unoccupied antibonding state may arise from the excited state \(4s\) of \(Zn^{++}\). This state transforms according to the \(a_{1g}\)-irreducible representation of \(O_h\) and can be coupled to the \(F^-\)-ligand state \(\chi\) \((a_{1g})\) to form a bonding-antibonding pair in which only the bonding state is occupied. It can be shown that in this case (see Appendix) \(\sigma^a\) remains unchanged with regard to (26), whereas \(\sigma^p\) has an additional contribution given by:

\[
\sigma^p_{xx} \text{(cov.)} = -\frac{4e^2 \hbar^2}{Am^2 c^2} \langle 1/r^3 \rangle_0 \cdot \frac{1}{6} b^2 (a_{1g}) \tag{28}
\]

where \(b(a_{1g})\) is the covalency factor [17] specific to the \(a_{1g}\)-states. In the following it will be simply labelled as \(b\). Taking into account this contribution, the expressions used for numerical evaluations are:

\[
\sigma^p_{xx} = \sigma^p_{xx}(O) - \frac{2e^2 \hbar^2}{Am^2 c^2} \langle 1/r^3 \rangle_0 \cdot \frac{1}{3} b^2 , \tag{29}
\]

\[
\sigma^p_{zz} = \sigma^p_{zz}(O) ,
\]

where \(\sigma^p_{xx}(O)\) and \(\sigma^p_{xx}(O)\) are given by (21).

The overlaps in (29) and (21) will be restricted to outer shells, namely: 3d for \(Zn^{++}\), (3s, 3p) for \(K^+\) and \((2s, 2p)\) for \(F^-\).

The summation in (29) was taken over the following groups of neighbours: two \(Zn^{++}\) labelled \((1, 2)\) at \((0, 0, \pm ½)\), two \(F^-\) \((1, 2)\) at \((0, 0, \pm 1)\), four \(K^+\) \((1 - 4)\) at \((\pm ½, \pm ½, 0)\) and symmetry related positions, and eight \(F^-\) \((1 - 4)\) at \((± ½, 0, \pm ½)\) and symmetry related positions. The overlap properties which arise from the symmetry of the problem \((e.g., S_{10}^{2z, 2} = S_{10}^{2z, 2} \text{ for } Zn^{++}, \text{ etc.})\) allow to bring (29) to a form which reflects the contributions of different groups of neighbours:

\[
\sigma^p_{xx} = -\frac{2e^2 \hbar^2}{Am^2 c^2} \langle 1/r^3 \rangle_0 \cdot \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 \sqrt{3} S_{10}^{2z, 2} S_{10}^{2z, 2} + b^2/6 \right]_{2x Zn^{++}} + 4\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 S_{10}^{2z} S_{10}^{2z} \right]_{4x K^+}
\]

\[
+ 2\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 S_{10}^{2z} S_{10}^{2z} \right]_{2x F^-}
\]

\[
+ 4\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} + S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 S_{10}^{2z} S_{10}^{2z} \right]_{2x F^-}
\]

\[
+ S_{20}^{2z, 2} + S_{20}^{2z, 2} + S_{20}^{2z, 2} + S_{20}^{2z, 2} - 2 S_{20}^{2z, 2}
\]

\[
- 2\left( S_{20}^{2z} S_{20}^{2z} + S_{20}^{2z} S_{20}^{2z} \right)_{8x F^-} \right) \tag{30}
\]

The indices 1 or 2 in each square bracket signify the nucleus at position 1 or 2 in each group according to the previous notation.

Overlap integrals are usually reported in terms of \(S^\pi, S^\sigma\) or \(S^h\), (17) and (18). Since in general the \(z\)-axis of the crystal frame used to write the ionic functions does not coincide with the vector between two nuclei, we made the necessary transformations to express different \(S^\tau\) in terms of these standard overlaps. We give the result directly for \(A \sigma^p\) and \(\sigma^p\):

\[
A \sigma^p = \frac{4e^2 \hbar^2}{Am^2 c^2} \langle 1/r^3 \rangle_0 \cdot \left[ \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 \sqrt{3} S_{10}^{2z} S_{10}^{2z} + b^2/6 \right]_{2x Zn^{++}} \right.
\]

\[
- \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{4x K^+}
\]

\[
+ \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{2x F^-}
\]

\[
+ \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{8x F^-} \right) , \tag{32}
\]

\[
\sigma^p = -\frac{8e^2 \hbar^2}{3 Am^2 c^2} \langle 1/r^3 \rangle_0 \cdot \left[ \left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} - 2 \sqrt{3} S_{10}^{2z} S_{10}^{2z} + b^2/6 \right]_{2x Zn^{++}} \right.
\]

\[
+ 2\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{4x K^+}
\]

\[
+ 2\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{2x F^-}
\]

\[
+ 4\left[ S_{10}^{2z, 2} + S_{10}^{2z, 2} \right]_{8x F^-} \right) \tag{33}
\]

Several qualitative conclusions can be inferred from (32) and (33):

- The overlap contribution to \(A \sigma^p\) may be small due to cancellation between different contributions. The stronger is the cancellation, the more important is the covalent contribution to \(A \sigma^p\).
For strong cancellation of overlap and weak covalency contributions, the calculated value of \( \Delta \sigma^p \) is strongly dependent on the accuracy of the overlap integrals (see further below).

- The ratio \( \Delta \sigma^p/\sigma^p \) depends on neither \( A \) nor \( 1/r^3 \). It is therefore well suited for comparison with the "semi-experimental" value obtained from line 5 of Table 1.

The overlap contributions \( \Delta \sigma^p (O) \) and \( \sigma^p (O) \) contained in (32) and (33) are obtained by setting \( b = 0 \).

In order to estimate their size we used the following sources of overlap integrals: \( F^-\)–\( F^- \) and \( F^-\)–\( K^+ \) overlaps were taken from [18] using the interpolation method proposed there; the \( F^-\)–\( Zn^{++} \) overlaps were assumed to be equal to those calculated for \( F^-\)–\( Ni^{++} \) in KNiF\(_3\) [17]. The distances between different nuclei in KNiF\(_3\) and KZnF\(_3\) are practically the same since the unit cell dimensions are \( a = 4.014 \) Å and \( a = 4.055 \), respectively. The following numbers were used: \( S^\sigma^p = 3.77 \), \( S^\sigma^e = 6.39 \) for \( F^-\)–\( Zn^{++} \), \( S^\sigma^e = 1.379 \), \( S^\sigma^e = 5.546 \), \( S^\sigma^e = 4.354 \) for \( F^-\)–\( K^+ \) and \( S^\sigma^e = 2.153 \), \( S^\sigma^e = 6.674 \), \( S^\sigma^e = 3.824 \) for \( F^-\)–\( F^- \). All these values should be multiplied by \( 10^{-2} \).

Using \( 1/r^3 \) from [4] and inserting in (32) to (33) the appropriate values of the overlaps one obtains: \( \Delta \sigma^p (O) = -1.6 \times 10^{-17} 1/A, \sigma^p (O) = -1.7 \times 10^{-15} 1/A \). The overlap contributions due to the two \( F^- \) at \( 0, 0, \pm 1 \) were entirely negligible. The expressions for the diamagnetic parts which correspond to (32)–(33) are not given here for space reasons. They give:

\[
\Delta \sigma^d (O) = 0.5 \text{ ppm}, \quad \sigma^d = 1.6 \text{ ppm}.
\]

As long as one neglects the covalent contribution, the following situation emerges:

- the diamagnetic overlap contributions to \( \Delta \sigma \) and \( \sigma \) can safely be neglected as expected [15, 16].
- the ratio \( \Delta \sigma^p (O)/\sigma^p (O) \) obtained with the above mentioned overlap values is at variance with regard to sign and magnitude with the semiexperimental value of Table 1 which is \(-7.3 \times 10^{-2}\).

Therefore it seems that the covalent contribution cannot be neglected. An evaluation of \( b \) can be done if the ratio \( \Delta \sigma^p/\sigma^p \) as given by (32) and (33) is set equal to the semiexperimental value \((-7.3 \times 10^{-2})\). One obtains \( b = 0.13 \).

Such a value is not unreasonable since in the closely related compound KNiF\(_3\), covalency factors \( b^+ \) and \( b^e \) of 0.175 and 0.285 were obtained (see [17]).

On the other hand, it should be noted that moderate changes of overlap values may significantly alter the result. As an example we consider the case where the \( F^-\)–\( F^- \) overlaps are uniformly increased by 15% and the \( F^-\)–\( Zn \) and \( F^-\)–\( K \) overlaps are decreased by 15%. In this case \( \Delta \sigma^p (O)/\sigma^p (O) \approx -0.1 \) and therefore covalency no longer needs to be invoked to explain the "semi-experimental" result. Such uncertainties may easily arise in overlap calculations and therefore we face the fact that for weakly covalent compounds in which \( \Delta \sigma^p \) is small it is difficult to estimate the covalency contribution only from chemical shift data. In the case of KZnF\(_3\), however, there exist NQR data which strongly indicate that covalency plays an important role. By NQR measurements on the \( ^{19}\text{F} \)-nuclei in KZnF\(_3\) [6] it was found that the EFG at the \( F^- \)-site is \( V_{zz} = + (7.7 \pm 1.7) 10^{17} \text{ cm}^{-2} \). We calculated \( V_{zz} \) (see Appendix) using the same procedure as for \( \sigma \) and obtained

\[
V_{zz} = V_{zz} (O) + \frac{4}{3} e (1/r^3) \left[ b^2 + 2 \sqrt{6} S^\partial^0 \right].
\]

where \( V_{zz} (O) \) is given by (A12).

Neglecting the covalent contribution \( (b = 0) \) and using the same values of overlaps as for \( \sigma \) one obtains the overlap contribution to \( V_{zz} \): \( V_{zz} (O) \approx -10^{17} \text{ cm}^{-2} \). On altering the value of the overlaps in the same way as was done tentatively above, the value of \( V_{zz} \) becomes even smaller. Therefore we conclude that a covalent contribution is essential to explain the experimental value of the EFG. As can be seen from (34) the covalent contribution is increasing the value of \( V_{zz} \) as is required by the experimental result. Unfortunately we have no knowledge of the overlap integral \( (F^-\)–\( Zn \)) \( S^0 \) in (34) and therefore we cannot evaluate \( V_{zz} \) using \( b \) obtained from the chemical shift data.

Conclusions

The anisotropy \( \Delta \sigma \) of the fluorine chemical shift in KZnF\(_3\) is small compared to \( \sigma \) and \( \sigma \) on the absolute scale. The main part (57%) of \( \Delta \sigma \) stems from closed shell electrons of neighbour ions ("geo-
metrical contribution”). This contribution is particularly important for KZnF$_3$ because of the filled 3d shell of Zn$^{++}$. In other ionic fluorides which have no ions with filled d shells the “metrical contribution” is much weaker, in MgF$_2$, e.g., it contributes only 15% to $\Delta \sigma$ [4].

The remaining part of $\Delta \sigma$ as well as of $\bar{\sigma}$ is mainly paramagnetic and reflects the departure of the wavefunctions from their purely ionic form, e.g., through covalent mixing of wavefunctions on neighbouring ions. As long as covalency is assumed to give rise to bonding and antibonding states which both are fully occupied the covalency factor does not appear explicitly in the formula for $\Delta \sigma^p$ and $\bar{\sigma}^p$. In such a case $\Delta \sigma^p$ and $\bar{\sigma}^p$ depend only on overlap integrals between wavefunctions on neighbouring ions (“overlap contribution”). The result is then essentially equivalent to that obtained by using orthogonalized ionic functions (Löwdin's method) and not invoking at all the idea of covalent mixing.

Only bonding states with empty or partially filled antibonding counterparts bring a contribution to $\Delta \sigma^p$ which contains explicitly the covalency strength. The influence of such states to $\bar{\sigma}^p$ is, in general, much weaker. This is probably the reason why in many treatments of averaged chemical shifts in ionic crystals Löwdin’s method was considered to be adequate [4, 15, 16]. When applied to KZnF$_3$ Löwdin’s method allows a reasonable qualitative explanation of the small value of $\Delta \sigma^p$: overlap contributions from different neighbour ions tend to cancel each other.

Our calculations indicate that Löwdin’s method is not sufficient to explain the experimental values of $\Delta \sigma$ and $\bar{\sigma}$ in KZnF$_3$ and that a covalent contribution from a (partially) occupied bonding state which has an empty antibonding counterpart needs to be taken into account. An estimate based on the “semiempirical” value of $\Delta \sigma^p/\bar{\sigma}^p$ gives a value for the respective covalency factor of $b = 0.13$.

An independent confirmation of this conclusion comes from the EFG at the F$^-$-site determined by $^{20}$F NQR in KZnF$_3$[6]. Neither its sign nor its magnitude can be explained if only Löwdin’s orthogonalized wavefunctions, or filled bonding and antibonding pairs of states are considered.

**Acknowledgements**

We are indebted to Prof. H. Ackermann for making available to us a large piece of a single crystal of KZnF$_3$ which was originally prepared by Prof. Leckebusch/Bonn for the NQR studies. R. G. gratefully acknowledges stipends from the Deutsche Kernforschungsgesellschaft in Karlsruhe and it is his pleasure to express his gratitude to Prof. K. H. Hauser and the Max-Planck-Society for hospitality.

**Appendix**

Here we shall outline the procedure used to calculate $\sigma$ (F) in the ZnF$_6$ fragment. It is based on a set of F$^-$-ligand wavefunctions used previously for estimating other physical properties in such a fragment [17, 19]. It allows an easy separation of the overlap- and covalent bonding contributions to $\Delta \sigma^p$ and $\bar{\sigma}^p$. The EFG at the F$^-$-site is calculated as well, using the same set of wavefunctions and approximations. The fluorines in the fragment are labelled as in [17] and [19]: F$_1$, F$_2$, F$_3$ on the x-, F$_4$, F$_5$ on the y-, and F$_6$ on the z-axis. F$_3$ is taken as the fluorine of interest. Hence overlaps of the form $S^p_{ij}$ are the same as $S^p_{ij}$ in the text. The central ion (Zn$^{++}$) as well as the ligand (6F$^-$) wavefunctions which transform according to the irreducible representations of $O_h$ are given in Tables 23–26 of [19]. The ligand wavefunction of type $S_r$ ($S_r = xy, xz, etc.$) belonging to the $r$-representation can be written

$$\chi (S_r, r) = [N (r)]^{-1/2} \sum_{Iz} A^p_I (S_r, r) \phi^p_I,$$

where $\phi^p_I = p_x (I), p_y (I), p_z (I)$. The amplitudes $A^p_I$ are directly taken from Table 26 of [19]. For example

$$\chi (xz, t_{2g}) = [N (t_{2g})]^{-1/2} \cdot [p_x (3) - p_x (6) + p_z (1) - p_z (4)]$$

with

$$N (t_{2g}) = \frac{1}{4} [1 - S_{3x}^x + 2 S_{3y}^y]^{-1} = \frac{1}{4} [1 + (S_{3x}^x - 2 S_{3y}^y) + (S_{3y}^y - 2 S_{3z}^z + ...]].$$

All overlap integrals appearing here are easily reduced to the usual overlaps $S^\alpha$, $S^{\alpha\alpha}$, $S^{\alpha\beta}$; e.g., $S_{3x}^x = S^{xx}$ for F$_3^-$–F$_6^-$. In the case of Zn$^{++}$ we assume that only 3d electrons participate in forming bonding-antibonding pairs. Therefore only $e_g$ and $t_{2g}$ ligand and central ion wavefunctions couple (see Table 24 of [19]).

$$\psi^b (S_r, r) = [N^b (r)]^{-1/2} \chi (S_r, r) + b (r) d (S_r, r),$$

$$\psi^a (S_r, r) = [N^a (r)]^{-1/2} [d (S_r, r) - a (r) \chi (S_r, r)]$$
Using (A6) for the diagonal populations $P_0^0$, (A10)
can be brought to the form

$$V_{zz} = V_{zz}^{(O)} + \frac{4}{5} e \langle 1/r^3 \rangle_{F_2} \cdot \frac{1}{2} [b^2(a_{1g}) + 2 \sqrt{6} S_{4\kappa} \cdot b(a_{1g})], \quad (A11)$$

where

$$V_{zz}^{(O)} = \frac{8}{3} e \langle 1/r^3 \rangle_{F_2} \cdot \|[S_{4\kappa}^0]^2 - (S_{2\kappa}^0)^2\|_{Zn^{++}}$$

+ $[(S_{1\kappa}^0)^2 - (S_{0\kappa}^0)^2 + (S_{0\kappa}^0)^2]_{K^+}$

$$- \frac{1}{4} [(S_{1\kappa}^0 + S_{0\kappa}^0)^2 + (S_{1\kappa}^0)^2]_{K^-} \quad (A12)$$

$V_{zz}^{(O)}$ has the same sources of contributions as $\sigma_{zz}^{(O)}$. As can be seen from (A7) and (A11) the unfilled antibonding state $A_{1g}$ makes a contribution which tends to increase both $\sigma_{zz}$ and $V_{zz}$.

[3] Ref. [1], Table 5.4.