Trace determination and pressure estimation of fluorine $F_2$ caused by irradiation damage in minerals and synthetic fluorides

Vinicius R. Celinski[a], Michael Ditter[b], Florian Kraus[c], Franz Fujara[b], and Jörn Schmedt auf der Günne[a]

Abstract: Irradiated alkali and earth alkali halides can form metal colloids and halogen molecules, which stay trapped inside the crystal. In this paper we provide $^{19}$F NMR evidence of trapped $F_2$ fluids in heavy ion bombarded synthesized LiF crystals as well as in a variety of the mineral Villiaumite (NaF). This is the 2nd mineral in which $F_2$ is unambiguously detected in nature. The trace quantification of the latter is in the order of magnitude of $10^{-6}$ mol/g. Pressures and densities of the $F_2$ fluids are estimated based on the theory of nuclear spin relaxation in dilute gases.

Introduction

Many insulators are ionic crystalline materials. It is known for a long time now, that defects in such materials can be generated by ionizing photon or particle irradiation. The radiation may stem from a natural environment (e.g. cosmic radiation or radioactive atoms in rocks) or from a more or less controlled one as in a nuclear facility along with its radioactive waste, a fusion reactor, a particle accelerator or a laser. For instance, a CaF$_2$ crystal can be used as an optical window that is subjected to high-energy radiation of a laser or as a scintillator. A salt dome for the disposal of radioactive waste will inevitably be exposed to nuclear radiation and is intended to be safe for disposed containers for thousands of years. Recently, Villiaumite (NaF) was found to be the dominant fluoride species in zircaloy cladding waste, which results in large amounts from removing zircaloy cladding from nuclear fuel rods.

Alkali halides feature a large band gap, making them not only excellent electrical insulators, but also transparent to light over a wide frequency range. In this respect LiF stands out for being one of the best materials for transmission of vacuum UV light. For these reasons it is merchandised in the form of mirrors, optical windows and lenses for various purposes. Furthermore, it finds use in thermoluminescent dosimeters and has a potential use as a thermal neutron detector in both fusion and fission nuclear reactors. As far as heavy ion induced defects are concerned LiF is one of the best studied ionic crystals.

The formation of halogen bubbles and metallic colloids are well known as a result of irradiation of alkali halides. In neutron-irradiated LiF these cavities were assumed to contain molecular $F_2$, which was evidenced by $^{19}$F NMR. After swift ion irradiation swelling has been reported as a reaction to an increased volume, among other crystals, also in LiF. The formation of micron-sized $F_2$ bubbles has already been observed in CaF$_2$ by atomic force microscopy, where a pressure of the $F_2$ fluid was estimated to be around 50 MPa. The occurrence and quantification of $F_2$ in the natural mineral "Antozonite", a variant of fluorite, suggested its occurrences to originate due to natural radioactivity. Recently, attention was drawn to the stability of polyfluoride anions and the existence of $F_5$ in a neon matrix.

In the present work we intend to provide evidence of the trapped $F_2$ fluid and quantify its amount in a further natural mineral as well as in heavy-ion-bombarded synthetic fluorides. Is it possible to estimate pressure and density of the fluid inside the formed cavities as was done in the case of trapped H$_2$ in irradiated LiH? Do the molecules feature the expected isotropic motion as in a fluid state in spite of the supposed small size of the cavities?

Results and Discussion

$^{19}$F NMR quantification

The $^{19}$F NMR spectra of the studied crystals are shown in Fig. 1. The amounts of $F_2$ fluid inside the cavities of the samples was determined by quantitative $^{19}$F NMR experiments and is gathered in table 1. The trace determination of $F_2$ in the mineral Villiaumite by $^{19}$F NMR is the second direct evidence of elemental fluorine in nature. We speculate that its formation must also derive from the effects of radiation arising from nearby radioactive minerals, as in the case of the mineral "Antozonite", where elemental fluorine in nature was detected for the first time.
Maximum fluid density in crystals damaged by irradiation

We aim at determining the upper limit for the density of an F\textsubscript{2} fluid in a cavity formed after irradiation. For that we assume that there is F\textsubscript{2} diffusion neither into nor out of the cavities after irradiation damage has occurred. In this manner we determine a maximum F\textsubscript{2} fluid density \( \rho_{F_2,\text{max}} \) can be formed in a crystal containing stoichiometric amounts of fluoride (e.g. NaF) after being damaged by irradiation:

\[
\rho_{F_2,\text{max}} = \frac{Z_{\text{fluoride}}}{V_{UC} \cdot N_A}
\]

where \( Z_{\text{fluoride}} \) is equal to the number of fluoride ions per unit cell, \( V_{UC} \) the unit cell volume, \( V_A \) the volume of the formed material after irradiation other than the F\textsubscript{2} fluid (e.g. solid Na) and \( N_A \) the Avogadro constant. The maximum fluid densities \( \rho_{F_2,\text{max}} \) of newly formed F\textsubscript{2} after irradiation damage of the studied crystals were calculated according to equation 1 and can be found in table 1. We deliberately set \( V_A = 0 \), corresponding to a scenario where the extra formed material diffuses away from the bubble towards the crystal surface.

**Table 1.** Amount \( n \) and mass \( m \) of F\textsubscript{2} per unit mass of sample, \( T_1 \) relaxation time, densities \( \rho \) and pressures \( p \) of F\textsubscript{2} in fluorides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>F\textsubscript{2} ( m/\text{mol} )</th>
<th>F\textsubscript{2} ( m/\text{mg} )</th>
<th>( T_1 ) (ms)</th>
<th>( \rho_{\text{calc}} ) ( (\text{mol cm}^{-3}) )</th>
<th>( \rho_{\text{max}} ) ( (\text{mol cm}^{-3}) )</th>
<th>( \rho_{F_2,\text{max}} ) ( (\text{MPa}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villiaumite (NaF)</td>
<td>0.0008±0.0012</td>
<td>0.001</td>
<td>15±1.4</td>
<td>0.014±0.0012</td>
<td>0.014±0.0012</td>
<td>33.6±6.7</td>
</tr>
<tr>
<td>Antozonite (CaF\textsubscript{2})</td>
<td>0.0001</td>
<td>0.002</td>
<td>1.4</td>
<td>0.030</td>
<td>0.004</td>
<td>32.3±5.6</td>
</tr>
<tr>
<td>LiF ( (1 \times 10^{-2}) )</td>
<td>0.005</td>
<td>0.1</td>
<td>1.3</td>
<td>0.030</td>
<td>0.004</td>
<td>32.3±5.6</td>
</tr>
<tr>
<td>LiF ( (2 \times 10^{-2}) )</td>
<td>0.005</td>
<td>0.1</td>
<td>1.3</td>
<td>0.051</td>
<td>0.011</td>
<td>32.3±5.6</td>
</tr>
<tr>
<td>F\textsubscript{2} ( (0.1-0.2) )</td>
<td>0.005</td>
<td>0.1</td>
<td>1.3</td>
<td>0.051</td>
<td>0.011</td>
<td>32.3±5.6</td>
</tr>
</tbody>
</table>

\[ n(F_2)/m(\text{mol})/ (\text{mmol g}^{-1}) \]

\[ m(F_2)/m(\text{total})/ (\text{mg g}^{-1}) \]

\[ T_1 \] (ms) and \( \rho_{\text{calc}}/\rho_{\text{max}}/\rho_{F_2,\text{max}}/ \] (mol cm\(^{-3}\))

\[ \rho_{F_2,\text{max}} = 3.3 \sqrt{\frac{V}{\pi \sigma_{ef}}} \frac{c^2 \beta T}{4} \]

\[ k_{lit} = \left( \frac{T_1}{\rho} \right)^{3/2} \]

\[ \rho_{\text{calc}} = \frac{T_1 \cdot \rho^{(3/2)}}{k_{lit}} \]

F\textsubscript{2} fluid density and pressure inside the cavities by \( ^{19} \text{F} \) NMR

Based on the assumption that longitudinal relaxation of the \( ^{19} \text{F} \) NMR signal in F\textsubscript{2} molecules occurs mainly through the spin-rotation mechanism, there is a link between \( T_1 \) values and pressure (equations 2 and 3). In this case the ratio \( (T_1/\rho) \) shows a temperature dependence:35-38

\[
(T_1/\rho) = \frac{35}{4C^2 \beta T} \frac{V_{eff}}{\pi \sigma_{ef}}
\]

Here \( h \) is the reduced Planck constant, \( V \) the mean relative velocity of the molecules, \( \sigma_{ef} \) the cross section for the transfer of angular momentum during a collision, \( c \) the spin rotation constant with an experimental value of \( 157 \pm 2 \) kHz\(^{-1}\) that shows good agreement with the theoretical value\(^{37} \), \( \beta \) the molecular moment of inertia with an experimental value of \( 3.17 \times 10^{-46} \) kg m\(^2\) \( \cdot \) s\(^{-1}\), \( V \) the Boltzmann constant and \( T \) the temperature of the gas.

We denote that the longitudinal relaxation under the spin-rotation mechanism is field independent.\(^{39} \) Under these circumstances the value of \( k_{lit} \) is constant so that we define \( k_{lit} = (T_1/\rho)^{3/2} \)

\[ k_{lit} = \left( \frac{T_1}{\rho} \right)^{3/2} \]

Values for F\textsubscript{2} have been reported in literature (\( (T_1/\rho)_{lit} \)), where \( T_1 \) is the experimentally determined longitudinal relaxation time constant for \( ^{19} \text{F} \) and \( \rho \) the density of the F\textsubscript{2} gas.\(^{40} \) Here, the density \( \rho \) is calculated from the known pressure \( p \) with the help of second virial coefficients.\(^{41} \) Based on those values we can calculate the density \( \rho_{\text{calc}} \) of the F\textsubscript{2} molecules inside the cavities of the crystals under investigation, as in equation 4:

\[
\rho_{\text{calc}} = \frac{T_1 \cdot \rho^{(3/2)}}{k_{lit}}
\]

The values of \( \rho_{\text{calc}} \) can be converted to pressure values \( p \) as shown in 2 according to the F\textsubscript{2} equation of state.\(^{32} \) These values
are of the same order of magnitude as the pressure value of \( F_2 \) bubbles in an irradiated \( \text{CaF}_2 \) crystal that was determined to be around 50 MPa.\(^{16} \) Furthermore, the calculated maximum fluid densities inside a crystal after irradiation (equation 1) indicate a similar range, where such pressure values can be found. We note here that higher calculated maximum fluid densities would be achieved in a scenario where part of the extra formed material stays in the bulk \((\gamma_\omega > 0)\). Thus, we conclude that \( F_2 \) bubbles are present inside the studied samples, where \( F_2 \) is in a supercritical state at room temperature, its critical pressure being 5.2 MPa and its critical temperature 144.4 K.\(^{32} \)

At such high pressures the viscosity of supercritical \( F_2 \) might get close to that of liquid \( F_2 \) just below its critical temperature.\(^{42} \) The longitudinal relaxation time of liquid \( F_2 \) at different pressures has been determined to be around 70-100 ms.\(^{43} \) In the regime of dense gases the assumption about collisions is not valid anymore and the density of the gas needs to be multiplied by a correction term.\(^{39,44} \) Even though this new density term shows a similar temperature dependence as in the case of dilute gases, strictly speaking equation 3 does not hold any longer. However, it still seems to be a fair approximation to estimate the order of magnitude of \( F_2 \) fluid pressure inside the crystals, since there exists no data on relaxation rates of \( F_2 \) at such high pressures. For instance, the prediction of \((T_1/\rho)\) of hydrogen gas at around 300 MPa is underestimated by a factor of 2 as compared to experimental data.\(^{44} \) An underestimation of \((T_1/\rho)\) translates into higher densities and therefore even higher pressures. According to the concept in section 0 this would be possible if part (or all) of the formed material other than \( F_2 \) (in our cases either metallic lithium, sodium or calcium) would stay inside the bulk.

Transverse relaxation and linewidth
Spins that relax under the spin–rotation mechanism feature a \( T_1 \) that is not dependent on the field.\(^{38} \) We tested that for the \( F_2 \) signal in “Antozonite” and determined the same value within experimental error. Moreover, it is also expected that \( T_1 = T_2 \). We determined \( T_2 \) values with a spin-echo\(^{22} \) \((T_2 = 9.6 \pm 0.2)\) ms as well as with the Carr-Purcell-Meiboom-Gill (CPMG)\(^{23} \) pulse sequence \((T_2 = 8.7 \pm 0.2)\) ms, both being similar to each other but smaller than \( T_1 \).

At higher signal to noise ratios one can see weak spinning side bands (Fig. 2), which are typical for solids and depend on the anisotropy of interactions. The lineshape of the \( F_2 \) signal in “Antozonite” can be deconvoluted by two peaks that feature a similar \( T_1 \) and practically the same chemical shift. The broadening of the linewidth of the narrow signal (around 250 Hz) can be explained by its spin–spin relaxation time \( T_{\alpha} \). The smaller and broader peak, however, features a linewidth around three times broader than the narrow peak, indicating the influence of another interaction.

The dipole-dipole interaction between the two fluorine atoms in \( F_2 \) is around -36.4 kHz, if one assumes a distance of 1.43 Å. If \( F_2 \) would be static, this would lead to many side bands under the current experimental conditions (sample spinning frequency \( \nu_s = 10 \text{ kHz} \)). On the other hand, fast molecular tumbling, as in a fluid, is able to completely average out this interaction. The presence of weak side bands is an indication that the truth might lie somewhere in between. We therefore hypothesized a residual dipole-dipole interaction. If this is the case, one might be able to excite double-quantum coherences.

Double-quantum excitation and size of the bubbles
The normalized\(^{27} \) double-quantum build up curve of the \( F_2 \) NMR signal in “Antozonite” is shown in Fig. 3. As discussed above, the successful excitation of double-quantum coherence is evidence of a residual dipole-dipole coupling. The normalized intensity is expected to reach a plateau at the value of 0.5 for a 2-spin system with increasing excitation time \( T_{\text{exc}} \). However, the experiment levels out at a value slightly higher than 0.1. We conclude that only part of the \( F_2 \) molecules features an anisotropic motion and contributes to the excitation of double-quantum coherence (actually \( 2n+2 \) quantum orders). The remaining ones do not contribute to the latter due to isotropic molecular tumbling, but still contribute to the reference signal through coherence transfer pathways of the order \( 4n \), with \( n \in N \). The amplitude of the 2-spin simulation was scaled down in order to fit the experimental data. From that fit we extracted the value of \((350 \pm 150)\) Hz for the residual dipole-dipole coupling.

The self-diffusion coefficients of liquid \( F_2 \) at different temperatures have been determined.\(^{43,45,46} \) Linear extrapolation to room temperature gives a value of the order of \( 1 \times 10^{-9} \text{ m}^2/\text{s} \). We therefore expect the \( F_2 \) fluid to have many encounters with the walls during an NMR experiment at room temperature, if the cavity is in the sub-micrometer range.

Based on the findings above, we propose a rough model where \( F_2 \) molecules are confined in tiny cavities. As a consequence of the non-fully isotropic motional tumbling in some of these cavities the intermolecular dipole-dipole interaction is not entirely averaged out. However, the measurement gives evidence of different kinds of cavities. The majority of the cavities allows for isotropic motion which leads to a complete suppression of the

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**Figure 2.** \(^{19} \text{F} \) MAS NMR spectrum of “Antozonite” (CaF\(_2\)) featuring side bands, which are typical for the MAS spectra of solids. Acquired at a sample spinning speed of 5 kHz.
dipole-dipole interaction of the F\(_2\) molecules therein. From the normalized double-quantum build up curve (Fig. 3) we estimate that 1 out of 5 molecules is subjected to a hindered motion.

![Graph showing normalized double-quantum build up curve for F\(_2\) molecules.](image)

**Figure 3.** Experimental normalized\(^{20}\) double-quantum build up curve of the F\(_2\) signal in “Antozone” (squares) as a function of the excitation time and a 2-spin simulation (line) with a dipole-dipole coupling of 350 Hz; sample spinning frequency of 10 kHz; error bars were estimated from experimental data.

Conclusions

In this contribution we have successfully detected the \(^{19}\)F NMR signal of F\(_2\) fluid in the natural mineral Villiaumite (NaF) as well as in heavy-ion-irradiated synthetic LiF crystals. This is in accordance with previous findings where the formation of F\(_2\) bubbles has been identified after irradiation. We were able to quantify not only the amount of F\(_2\) in the synthetic crystals, but also determine a trace of F\(_2\) (~10\(^{-6}\) mol/g) in Villiaumite. The presence of polyfluoride anions was not indicated by extra unassignable NMR peaks.

The pressure of F\(_2\) inside the cavities was estimated based on the theory of nuclear spin relaxation of dilute gases. Since the determined pressures are of the order of magnitude of 100 MPa we conclude that F\(_2\) is in a supercritical state at room temperature, featuring corresponding high densities. The maximum fluid density expected in irradiation-damaged crystals is of the same order as the estimation of F\(_2\) densities.

We observed weak side bands during MAS NMR experiments and were able to excite double-quantum coherences thereby extracting a value for the residual dipole-dipole coupling. Polarization transfer between the molecules and lattice fluoride ions could not be observed. From that we conclude that part of the trapped molecules feature an anisotropic motion. We believe that our contribution helps to understand the mechanism of defect formation in irradiated crystals. The size and aspect ratio of cavities could possibly influence the properties of the crystals. Moreover, one might address the question of how much of the formed material other than F\(_2\) diffuses towards the surface and how much of it is interstitial. This could be important for radioactive waste disposal in salt domes, where a chemical reaction of the containers with a possible continuously formed halogen gas is not desired. Furthermore, it might also be significant for lenses that cannot be easily maintained and are exposed to irradiation, as for example on satellites.

**Experimental Section**

One of the LiF single crystals was irradiated with Pb ions at the UNILAC linear accelerator of the GSI Helmholtz Center in Darmstadt, Germany. The energy of Pb ions was 1.78 GeV with a fluence of 2x10\(^{12}\) ions cm\(^{-2}\). The other LiF single crystal was irradiated with Xe ions at the SIS synchrotron of the Darmstadt Center also in Darmstadt, Germany. The energy of Xe ions was 22.1 GeV with an ion fluence of 3x10\(^{11}\) ions cm\(^{-2}\). The mineral Villiaumite (NaF) stems from the Kola Peninsula in Russia and features a red color. The mineral “Antozone” (CaF\(_2\)) comes from Wölsendorf in Germany and features a black color.

Quantification, \(T_1\) saturation recovery and \(T_2\) inverse recovery NMR experiments were conducted at a magnetic field of 4.7 T on a Bruker Avance II-200 spectrometer equipped with a home-built 4 mm MAS probe working at the \(^1\)H frequency of 200.0 MHz. Spectra in Fig. 1 were acquired at a sample spinning speed of 10 kHz, except for the spectrum of “Antozone.” Spectra a and b in Fig. 1 were gained with a single pulse excitation experiment, while spectra c and d were gained with a spin-echo experiment. \(T_1\) saturation recovery, spin-echo\(^{20}\), CPMG\(^{21}\), single pulse excitation and double-quantum NMR experiments on “Antozone” were conducted at a magnetic field of 11.7 T on a Bruker Avance III-500 spectrometer equipped with a commercial 4 mm MAS probe working at the \(^1\)H frequency of 500.13 MHz. We used a Brent-corrected double-quantum experiment\(^{24,25}\) at a sample spinning frequency of 10 kHz, accumulating 128 transients/FID and the POST C-element\(^{26}\) with equal excitation and reconvension times that added up to 1.6 ms. The phase cycles were chosen as to satisfy a normalization approach described elsewhere.\(^{27}\) The single excitation experiment (Fig. 2) accumulated 1950 transients at a sample spinning frequency of 5 kHz with a repetition delay of 0.1 s. For all experiments the \(^1\)H resonance of 1% tetramethylsilane in CDCl\(_3\)served as an external secondary reference for the \(^{19}\)F resonance of neat CCl\(_4\)F using the \(\Xi\) values for \(^{19}\)F as reported by the IUPAC.\(^{28}\) The SIMPSON package (version 3.1.2) was used for simulations.\(^{29}\)

We determined the amount of F\(_2\) in the crystals by performing quantitative \(^{19}\)F NMR experiments for the F\(_2\) signal as well as for the signal originating from fluorine ions (1). Subsequently, the peak areas divided by the number of scans was used for the quantification.

**Table 2.** Acquisition parameters for the \(^{19}\)F-quantification by solid state NMR.

<table>
<thead>
<tr>
<th>Head (^1)H</th>
<th>Villiaumite (NaF)</th>
<th>LiF (3x10(^{11})Xe/cm(^2))</th>
<th>LiF (2x10(^{13}) Pb/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition delay (F(_2)) / s</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Repetition delay (F(^{-})) / s</td>
<td>8192</td>
<td>300</td>
<td>224</td>
</tr>
<tr>
<td>Number of scans (F(_2))</td>
<td>2081008</td>
<td>8192</td>
<td>4359</td>
</tr>
<tr>
<td>Number of scans (F(^{-}))</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The very aggressive nature of F\(_2\) leads to a chemical reaction with almost every container material. Moreover, even small amounts of water on the wall of a container will react with F\(_2\) to form HF, and several oxygen containing species. If the container is a typical laboratory glass, HF will eventually react with it to form SiF\(_4\) and again water, that can start the cycle once more until F\(_2\) is completely consumed. A polymer container (e.g. FEP,
PFA or PTFE) on the other hand enables the diffusion of F\(_2\) through its walls. From our experience, a sufficiently large number of repetitions of a \(^{19}\)F NMR single pulse excitation experiment can even provide evidence of trapped F\(_2\) in the polymer wall (not shown).\(^\text{30}\) We used the value for the longitudinal relaxation time \(T_1\) of F\(_2\) in accordance with literature: \(T_1\)(F\(_2\); 293 K; 100-200 kPa)=45 μs.\(^\text{31}\)

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**Keywords:** NMR, relaxation, radiation damage, double-quantum, Fluorine

[30] There is a discrepancy about the \(T_1\) value of F\(_2\) gas in literature. We chose to use the value determined in reference [31] and not the value from references [40,47], since the former showed the \(^{19}\)F NMR spectrum of F\(_2\) and thoroughly described the precautions taken to avoid the reaction of F\(_2\) with the wall of the container. The other authors did not report on the problematic handling of F\(_2\).
A trace quantification of elemental F\textsubscript{2} is provided in the mineral Villaumite NaF. This is the 2\textsuperscript{nd} mineral in which F\textsubscript{2} is unambiguously detected in nature.

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