Hyperfine fields at alkali impurities in Fe

Stefaan Cottenier
**Motivation**

*S. Cottenier and H. Haas, PRB 62 (2000) 461*
Motivation

** K. Nishimura et al., PRB 68 (2003) 012403 -- Beta-NMR/ON
Motivation
<table>
<thead>
<tr>
<th></th>
<th>$B_{hf}(T)$</th>
<th>isotope</th>
<th>method</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Na</td>
<td>-5.8</td>
<td>$^{24}\text{Na}$</td>
<td>$\beta$- and $\gamma$-LTNO</td>
<td>Severijns, Hyp. Int. 75 (1992) 331 Severijns, Physica B 194 (1994) 347</td>
</tr>
<tr>
<td>K</td>
<td>-6.5</td>
<td>$^{40}\text{K}$</td>
<td>TDPAD</td>
<td>Brandolini, Hyp. Int. 5 (1978) 127</td>
</tr>
<tr>
<td></td>
<td>-6.6</td>
<td>$^{41}\text{K}$</td>
<td>TDPAD</td>
<td>Lieb, Hyp. Int. 14 (1983) 177</td>
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<tr>
<td></td>
<td>-5.8</td>
<td>$^{43}\text{K}$</td>
<td>TDPAD</td>
<td>Lieb &amp; Haas, Hyp. Int. 20 (1984) 285</td>
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<tr>
<td></td>
<td>-15.7</td>
<td>$^{41}\text{K}$</td>
<td>TDPAC</td>
<td>Marmor, Bull. Am. Phys. Soc. 17 (1972) 87</td>
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<tr>
<td>Rb</td>
<td>+5.4</td>
<td>$^{83}\text{Rb}$</td>
<td>LTNO (suspicious)</td>
<td>Stone, Hyp. Int. 15/16 (1983) 313</td>
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<tr>
<td></td>
<td>$\geq +14.5$</td>
<td>$^{79}\text{Rb}$</td>
<td>NMR/ON (failed)</td>
<td>Delheij, TRIUMF Ann. Rep. 2004</td>
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<tr>
<td></td>
<td>+14.4</td>
<td>$^{83}\text{Rb}$</td>
<td>LTNO</td>
<td>Severijns (2006, priv. comm.)</td>
</tr>
</tbody>
</table>
### Experiment

<table>
<thead>
<tr>
<th></th>
<th>$B_{hf}(T)$</th>
<th>isotope</th>
<th>method</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>± 40.8</td>
<td>$^{119}\text{Cs}$</td>
<td>LTNO (as impl.)</td>
<td>Stone, Hyp. Int. 35 (1987) 821</td>
</tr>
<tr>
<td></td>
<td>+27.6</td>
<td>$^{133}\text{Cs}$</td>
<td>MOSS</td>
<td>De Waard, Hyp. Int. 5 (1978) 167</td>
</tr>
<tr>
<td></td>
<td>± 27.8</td>
<td>$^{136}\text{Cs}$</td>
<td>NMR/ON</td>
<td>De Waard, Phys. Lett. 29A (1969) 290</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 sites with smaller fields as well</td>
</tr>
<tr>
<td>Fr</td>
<td>±94.9</td>
<td>$^{208}\text{Fr}$</td>
<td>NMR/ON</td>
<td>Stone, Hyp. Int. 59 (1990) 461</td>
</tr>
<tr>
<td></td>
<td>±109-141</td>
<td>$^{221}\text{Fr}$</td>
<td>LTNO</td>
<td>Severijns, PRB 57 (1998) 11527 (review)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(various papers)</td>
</tr>
</tbody>
</table>

*Note: *
- Channeling as well, conjecture subst. site
- Higher fields immediately after impl. Wide resonance. Conjecture: vac.-ass. site
- Review: Stone, Hyp. Int. 84 (1994) 3
Technical issues

Framework: 
- Density Functional Theory
- PBE XC-functional
- APW+lo method (WIEN2k code)
- scalar relativistic + spin-orbit coupling

Numerical accuracy and significance of results guaranteed by:

- well-tested Brillouin zone sampling and basis set size
- Full relaxation of all atoms in the cell
- Fermi contact field, spin dipolar field, orbital field
- Large and tested supercell size
Technical issues

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Supercell concept
Supercell concept
Unrelaxed supercells

Impurity-impurity interaction vanishes from 32-atom cell onwards.

![Graph showing B_hf (T) vs. Impurity-impurity distance (a_0) and # atoms. The graph includes lines for Li, Na, K, and Rb, indicating the decrease in B_hf (T) as the distance and number of atoms increase.]
Unrelaxed supercells

Impurity-impurity interaction vanishes from 32-atom cell onwards.
Supercell selection

Unrelaxed supercells

Impurity-impurity interaction vanishes from 32-atom cell onwards.

“Fermi level accident” for Cs and Fr

🔹 Details on request
🔹 Disappears for Fr after relaxation

➡️ 64 atoms is very safe
➡️ Cs (and Fr ?) might be unreliable
Results

64-atom cell -- substitutional position

* smooth trend, except for Cs
* Cross-check: Sr agrees with experiment
* Rb: 1) previous calculation confirmed
  2) still disagreement with experiment
Results

64-atom cell -- substitutional position

- smooth trend, except for Cs
- Cross-check: Sr agrees with experiment
- Rb: 1) previous calculation confirmed
  2) still disagreement with experiment

The Rb that was experimentally studied does not sit at a substitutional site in pure bcc Fe.
Results

Verify interstitial sites

substitutional

[Graph showing $B_{hf}$ (T) vs. Li, Na, K, Rb, Cs, Fr, Sr with markers for exp and sub]
Results

Verify interstitial sites

substitutional  octahedral

![Diagram of substitutional and octahedral sites with atoms labeled Li, Na, K, Rb, Cs, Fr, Sr.](image)

Graph showing $B_{hf}$ vs. elements with data points labeled as 'exp' and 'sub'.

- exp
- sub
Verify interstitial sites

substitutional  octahedral

Results

\[ B_{hf} (T) \]

-100  -50  0  50  100  150

Li  Na  K  Rb  Cs  Fr  Sr

-100
-50
0
50
100
150

\( \text{exp} \)
\( \text{sub} \)
\( \text{octa} \)
Results

Verify interstitial sites

substitutional  octahedral  tetrahedral

\[ B_{hf}(T) \]

-100  -50  0  50  100  150

Li  Na  K  Rb  Cs  Fr  Sr

exp  sub  octa  tetra
Results

Smooth trends, broken by Cs only
Sr is definitely not on one of these interstitial sites
Rb is unlikely to be on one of these sites either

But... lowered symmetry ➔ EFG ➔ combined interaction
Results

Message to experimentalists:

Verify whether your data allow for these combined interactions!
(consider all possible angles between $B_{hf}$ and $V_{zz}$ in polycrystal)
Results

Another of the (many) possibilities: Rb traps a vacancy

8 @ 2.847 Å
8 @ 4.931 Å
12 @ 4.026 Å
6 @ 5.694 Å
24 @ 6.366 Å
Another of the (many) possibilities: Rb traps a vacancy

Results

7
8 @ 2.847 Å
12 @ 4.026 Å
8 @ 4.931 Å
6 @ 5.694 Å
24 @ 6.366 Å

6 @ 2.548 Å
6 @ 3.081 Å
2 @ 3.610 Å
6 @ 3.703 Å
12 @ 4.242 Å
6 @ 4.709 Å
Results

Another of the (many) possibilities: Rb traps a vacancy

\[
\begin{align*}
7 & \quad 8 @ 2.847 \text{ Å} \\
& \quad 12 @ 4.026 \text{ Å} \\
& \quad 8 @ 4.931 \text{ Å} \\
& \quad 6 @ 5.694 \text{ Å} \\
& \quad 24 @ 6.366 \text{ Å}
\end{align*}
\]

\[
\begin{align*}
B_{hf} & \quad V_{zz} \\
(// B_{app}) & \quad (\text{Tesla})
\end{align*}
\]

\[
\begin{align*}
\text{sub} & \quad -33 & \quad 0.0 (001) \\
\text{octa} & \quad +61 & \quad +6.9 (001) \\
\text{tetra} & \quad +62 & \quad -3.8 (001) \\
\text{vacancy} & \quad +30 & \quad -32.6 (111) \\
\text{(Tesla)} & \quad (10^{21} \text{ V/m}^2)
\end{align*}
\]

\[
\begin{align*}
6 @ 2.548 \text{ Å} \\
6 @ 3.081 \text{ Å} \\
2 @ 3.610 \text{ Å} \\
6 @ 3.703 \text{ Å} \\
12 @ 4.242 \text{ Å} \\
6 @ 4.709 \text{ Å}
\end{align*}
\]

polycrystal: all possible angles between \( B_{hf} \) and \( V_{zz} \)
Conclusions
Conclusions
Conclusions

No problems for:

- the light alkali (Na, K)
- Sr

Very likely substitutional

Note: no experiment for Li

<table>
<thead>
<tr>
<th></th>
<th>exp</th>
<th>sub</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>---</td>
<td>-1.7</td>
</tr>
<tr>
<td>Na</td>
<td>-5.8</td>
<td>-6.6</td>
</tr>
<tr>
<td>K</td>
<td>(-6.6, -15.7)</td>
<td>-12.0</td>
</tr>
<tr>
<td>Sr</td>
<td>-23.8</td>
<td>-27.8</td>
</tr>
</tbody>
</table>
Message for Rb:

- In none of the experiments so far it was at the substitutional site
- When analyzing and/or planning LTNO and NMR/ON, the characteristics of these 4 calculated sites can be helpful

Note: $^{83}\text{Rb} \Rightarrow 0.196 \text{ b}$
**Message for Cs and Fr:**

- *Cs (and Fr?) are very sensitive to details, in calculations as well as in experiment.*
- Especially *Cs might not follow the trend of the other alkali.*
- Indications that *Cs might sit non-substitutionally* ($^{136}$Cs: $Q=+0.225$ b)
- NMR/ON value for $^{208}$Fr ($Q=+0.004$ !) compatible with sub and octa.
  $^{221}$Fr with higher $B_{hf}$ has $Q=-1.00$ : also Fr non-substitutional?
General messages:

• Surprisingly many issues are not yet settled for these simple impurities.

• NMR/ON on isotopes with $Q \neq 0$ and with sign measurement would be very helpful.

• The present calculations give the necessary information to carry out such experiments efficiently.
General messages:

• Surprisingly many issues are not yet settled for these simple impurities.

• NMR/ON on isotopes with $Q \neq 0$ and with sign measurement would be very helpful.

• Past: experiment benchmark for theory
  Present: theory guideline for experiment
Conclusions

Side-line stories:

- Fermi level accident
- Nearest neighbour distances
- Individual trends of Fermi, dipolar and orbital fields
- EFG analysis
- Estimates for Cs and Fr with vacancy
“Fermi level accident”

Substitutional Na in Fe

Contact field is related to spin density.

Na 3s-up DOS
Na 3s-dn DOS
Na 3s-up integrated DOS
Na 3s-dn integrated DOS

Difference of these integrals, evaluated at the Fermi energy:

-0.010 \mu_B

This corresponds to the -6.5 T contact field (both must have same sign)
"Fermi level accident"

Substitutional Rb in Fe

Based on sequence of levels in free atoms:

Rb-5s is closer to the Fermi level (determined by Fe-3d) than Na-3s.

-0.009 $\mu_B$
“Fermi level accident”

Substitutional Cs in Fe

 Cs-6s-down is at the Fermi level: spin density highly sensitive to any small change!

$+0.019 \mu_B$
“Fermi level accident”

Substitutional Fr in Fe

The same applies to Fr-7s-down.

-0.008 \( \mu_B \)
“Fermi level accident”

Relaxed substitutional Fr has 7s-dn just below EF (it’s above EF before relaxation). This is the same situation as for Li-Na-K-Rb. The only one with the s-dn peak above EF is Cs (relaxed and unrelaxed).

- Cs and Fr are inherently sensitive to small details, also experimentally.
- Relaxed Fr follows the trend of the others, Cs not (but Fr can be potentially disturbed).
Neighbour relaxation

- Only for substitutional Li there is a (negligible) inward relaxation
- In all other cases, neighbours move outwards
- Beyond 3.5 Å, changes are small
- Relaxation increases with Z, but not dramatically

(horizontal dashed lines are pure Fe distances)
Contact, orbital and dipolar fields

- $B_{\text{tot}}$
- $B_{\text{Fermi}}$
- $B_{\text{orb}}$
- $B_{\text{dip}}$

Contact, orbital and dipolar fields
## EFG analysis

<table>
<thead>
<tr>
<th>Rb-atom</th>
<th>Fe-neighbours</th>
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<tbody>
<tr>
<td>Rb-3d</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
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<td></td>
<td>-0.1</td>
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<tr>
<td>Rb-4s</td>
<td>0.0</td>
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<tr>
<td>Rb-4p</td>
<td>-2.3</td>
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<tr>
<td></td>
<td>9.7</td>
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<tr>
<td></td>
<td>-0.6</td>
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</table>

Total = +6.8  

Rb at octahedral site
Cs and Fr with vacancy: estimates

- Calculating the vacancy site is very time-consuming
- Relaxed Rb-case shows high regularity: neighbourhood is the same as for RbFe\(_7\) with P-3m1 symmetry (5 inequivalent positions)

Quick calculations are now possible to estimate the hyperfine quantities:

<table>
<thead>
<tr>
<th></th>
<th>(B_{hf})</th>
<th>(V_{zz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb-supercell</td>
<td>+30.0</td>
<td>-32.6</td>
</tr>
<tr>
<td>RbFe(_7)</td>
<td>+14.0</td>
<td>-25.3</td>
</tr>
<tr>
<td>CsFe(_7)</td>
<td>+31.4</td>
<td>-52.9</td>
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<td>FrFe(_7)</td>
<td>+8.1</td>
<td>-105.3</td>
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