magnetic hyperfine interaction in solids

www.hyperfinecourse.org

1

magnetic hyperfine interactions in solids

The presence of a crystal lattice in a solid breaks the rotational invariance of space – which is required to get to the concept of |F> etc.

➔ different formalism needed.

The magnetic hyperfine field will have a fixed direction in space (not yet determined/specified which direction). Take the z-axis of your axis system along this direction.
(This means we work in a PAS for the dipole interaction – see later.)

Perturbation theory:

wave function for the point nucleus solid

$$E_{jj} = -\langle I|\hat{\boldsymbol{\mu}}_I|I\rangle \cdot \left\langle \psi_e^{(0)} \middle| \hat{\boldsymbol{B}}(\mathbf{0}) \middle| \Psi_e^{(0)} \right\rangle$$
$$= -\langle I|\hat{\boldsymbol{\mu}}_I|I\rangle \cdot \boldsymbol{B}(\mathbf{0})$$
$$= -\langle I|\hat{\mu}_{I,z}|I\rangle\, B(\mathbf{0})$$

nuclear wave function

2

2

magnetic hyperfine interactions in solids

The presence of a crystal lattice in a solid breaks the rotational invariance of space – which is required to get to the concept of |F> etc.

➔ different formalism needed.

The magnetic hyperfine field will have a fixed direction in space (not yet determined/specified which direction). Take the z-axis of your axis system along this direction.
(This means we work in a PAS for the dipole interaction – see later.)

Perturbation theory:

wave function for the point nucleus solid

$$E_{jj} = -\langle I|\hat{\boldsymbol{\mu}}_I|I\rangle \cdot \left\langle \psi_e^{(0)} \middle| \hat{\boldsymbol{B}}(\mathbf{0}) \middle| \Psi_e^{(0)} \right\rangle$$
$$= -\langle I|\hat{\boldsymbol{\mu}}_I|I\rangle \cdot \boldsymbol{B}(\mathbf{0})$$
$$= -\langle I|\hat{\mu}_{I,z}|I\rangle\, B(\mathbf{0})$$

computable by point-nucleus DFT codes

nuclear wave function

3

3

magnetic hyperfine interactions in solids

We don't know explicit expression for the nuclear wave functions – how to overcome ?

$$\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\hbar}\hat{\boldsymbol{I}}$$

$$\hat{\boldsymbol{I}} = \hat{I}_x\boldsymbol{e}_x + \hat{I}_y\boldsymbol{e}_y + \hat{I}_z\boldsymbol{e}_z$$

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \qquad \hat{I}_+|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I+1)}\,\hbar\,|I, m_I+1\rangle$$

$$\hat{I}_- = \hat{I}_x - i\hat{I}_y \qquad \hat{I}_-|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I-1)}\,\hbar\,|I, m_I-1\rangle$$

Rewrite the magnetic moment operator as a sum of operators for which the nuclear states are eigenfunctions – the eigenvalues depend on quantities that can be experimentally determined.

$$\hat{\mu}_{Ix} = \frac{\mu}{2I\hbar}\left(\hat{I}_+ + \hat{I}_-\right)$$
$$\hat{\mu}_{Iy} = \frac{\mu}{2I\hbar}\frac{1}{i}\left(\hat{I}_+ - \hat{I}_-\right)$$
$$\hat{\mu}_{Iz} = \frac{\mu}{I\hbar}\hat{I}_z$$

4

4

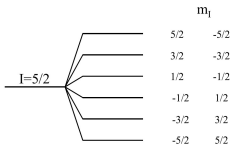
magnetic hyperfine interactions in solids

In this way, we can express the nuclear matrix element that we need in terms of the experimentally accessible quantities μ and I:

$$\langle m_I', I|\hat{\mu}_z|I, m_I\rangle = \frac{\mu}{I} m_I\, \delta_{m_I', m_I}$$

(i.e. we circumvent the lack of nuclear physics theoretical knowledge by using experimental input).

$$E_{jj}^{m_I} = -\frac{\mu m_I}{I} B_{hf}$$



m_I	
5/2	-5/2
3/2	-3/2
1/2	-1/2
-1/2	1/2
-3/2	3/2
-5/2	5/2
$g_I<0$	$g_I>0$

Equidistant:

$$E_{hf}^{m_I+1} - E_{hf}^{m_I} = -g_I\,\mu_N\,B_{hf} = \hbar\omega_L$$

5

5

Intermezzo: physical meaning of g_I

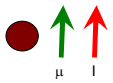
Two vector properties of the nucleus: I and μ

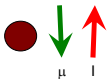
(μ is related to interaction with magnetic fields, I plays a role in the weak interaction)

They are related to each other by g_I: $\hat{\boldsymbol{\mu}} = \frac{g\,\mu_N}{\hbar}\hat{\boldsymbol{I}}$

The sign of g_I determines the orientation of μ w.r.t. I

Gyromagnetic ratio:
$\hat{\boldsymbol{\mu}} = \gamma\hat{\boldsymbol{I}}$
$\gamma = \frac{g\,\mu_N}{\hbar}$





6

6

magnetic hyperfine interactions in solids

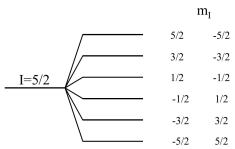
In this way, we can express the nuclear matrix element that we need in terms of the experimentally accessible quantities μ and I:

$$\langle m_I', I | \hat{\mu}_z | I, m_I \rangle = \frac{\mu}{I} m_I \delta_{m_I', m_I}$$

(i.e. we circumvent the lack of nuclear physics theoretical knowledge by using experimental input).

$$E_{jj}^{m_I} = -\frac{\mu m_I}{I} B_{hf}$$

computable



Equidistant:

$$E_{hf}^{m_I+1} - E_{hf}^{m_I} = -g_I \mu_N B_{hf} = \hbar \omega_L$$

7

magnetic hyperfine interactions in solids
the hyperfine field operator

Without derivation:

$$\boldsymbol{B}(\mathbf{0}) = -\frac{\mu_B \mu_0}{2\pi\hbar} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{L}_i}{r^3} \middle| \psi_e^{(0)} \right\rangle + \frac{\mu_B \mu_0}{4\pi} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{\sigma} - 3(\boldsymbol{\sigma} \cdot \boldsymbol{e}_r)\boldsymbol{e}_r}{r^3} \middle| \psi_e^{(0)} \right\rangle + -\frac{2\mu_B \mu_0}{3} \left\langle \psi_e^{(0)} \middle| \boldsymbol{\sigma}\, \delta(\boldsymbol{r}) \middle| \psi_e^{(0)} \right\rangle$$

8

8

magnetic hyperfine interactions in solids
the hyperfine field operator

Without derivation:

$$\boldsymbol{B}(\mathbf{0}) = -\frac{\mu_B \mu_0}{2\pi\hbar} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{L}_i}{r^3} \middle| \psi_e^{(0)} \right\rangle + \frac{\mu_B \mu_0}{4\pi} \left\langle \psi_e^{(0)} \middle| \frac{\boldsymbol{\sigma} - 3(\boldsymbol{\sigma} \cdot \boldsymbol{e}_r)\boldsymbol{e}_r}{r^3} \middle| \psi_e^{(0)} \right\rangle + -\frac{2\mu_B \mu_0}{3} \left\langle \psi_e^{(0)} \middle| \boldsymbol{\sigma}\, \delta(\boldsymbol{r}) \middle| \psi_e^{(0)} \right\rangle$$

- orbital contribution
- spin dipolar contribution
- Fermi contact contribution

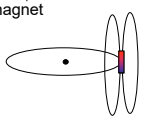
9

9

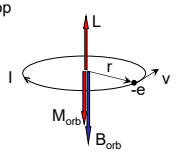
magnetic hyperfine interactions in solids
the hyperfine field operator

$B_{tot} = B_{dip} + B_{orb} + B_{Fermi}$

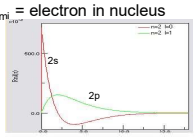
- B_{dip} = electron as bar magnet



- B_{orb} = electron as current loop



- B_{Fermi} = electron in nucleus



$$-\frac{2\mu_B \mu_0}{3} \left(|\psi_{e,\uparrow}(\mathbf{0})|^2 - |\psi_{e,\downarrow}(\mathbf{0})|^2 \right)$$

(+ other contributions from the atomic moments of neighbouring atoms -- Lorentz construction; too much detail for our purpose)

10

10

magnetic hyperfine interactions in solids
case studies

bcc-Fe

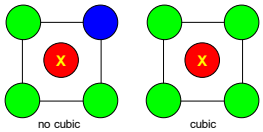
orbital hyperfine field:	9.6 T
dipolar hyperfine field:	-0.03 T
Fermi contact hyperfine field:	
1s+2s+3s (core):	-41.2 T
4s (valence):	-3.7 T
Sum:	**-35.3** T

11

11

magnetic hyperfine interactions in solids
symmetry properties

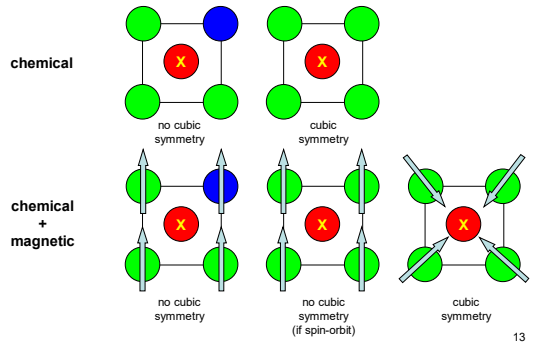
chemical



12

12

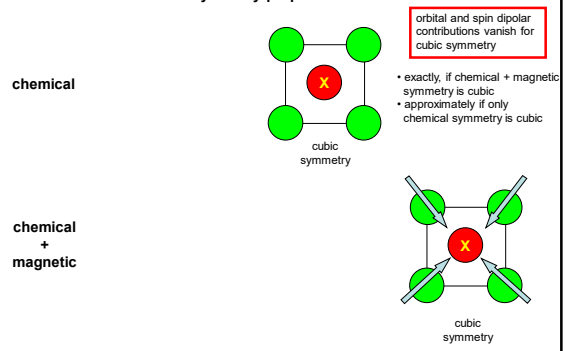
magnetic hyperfine interactions in solids
symmetry properties



13

13

magnetic hyperfine interactions in solids
symmetry properties



14

14

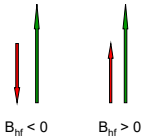
magnetic hyperfine interactions in solids
case studies

bcc-Fe

orbital hyperfine field:	9.6 T
dipolar hyperfine field:	-0.03 T
Fermi contact hyperfine field:	
1s+2s+3s (core):	-41.2 T
4s (valence):	-3.7 T
Sum:	**-35.3** T

What does the sign mean:

Orientation of the hyperfine field (vector) with respect to the spin moment (vector) of the atom



15

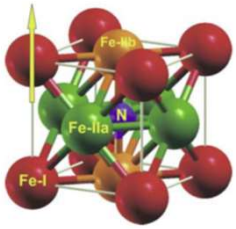
15

magnetic hyperfine interactions in solids
case studies

Fe_4N

chemical lattice:
Fe-I (cubic)
Fe-II (non-cubic)

magnetic lattice:
Fe-I (non-cubic)
Fe-IIa (non-cubic)
Fe-IIb (non-cubic)



Fermi contact hff			orbital hff			dipolar hff		
Fe-I	Fe-IIa	Fe-IIb	Fe-I	Fe-IIa	Fe-IIb	Fe-I	Fe-IIa	Fe-IIb
-29.7	-21.0	-21.1	3.7	0.4	2.7	0.0	3.0	-6.3

16

16

The hyperfine field on a Fe-nucleus in bcc Fe is -35.3 T.

Consider one atom of whatever element X as substitutional impurity in a bcc Fe matrix. What is the hyperfine field at the nucleus of X?

A) the same as for a Fe nucleus

B) slightly different from the value for a Fe nucleus

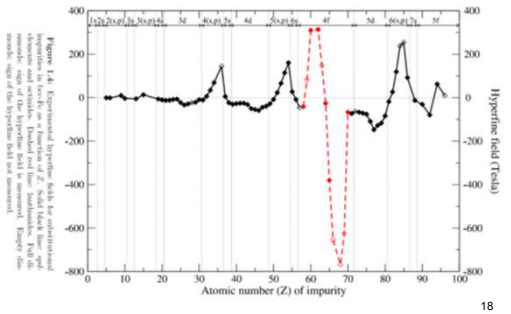
C) totally different

17

17

magnetic hyperfine interactions in solids
case studies

isolated substitutional impurities in bcc-Fe



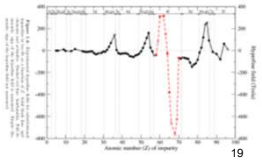
18

18

magnetic hyperfine interactions in solids
case studies

- 50 years of experimental work
- a repeated trend through every period of the periodic table
  - small and negative for s-groups
  - S-shape for d-block
  - rising from small and negative to large and positive in p-block
  - huge fields with positive/negative transition for f-block

➔ all this can be understood (not really the goal of this course)



19

19