

偏極RIビームを用いた β -NMR による物性研究

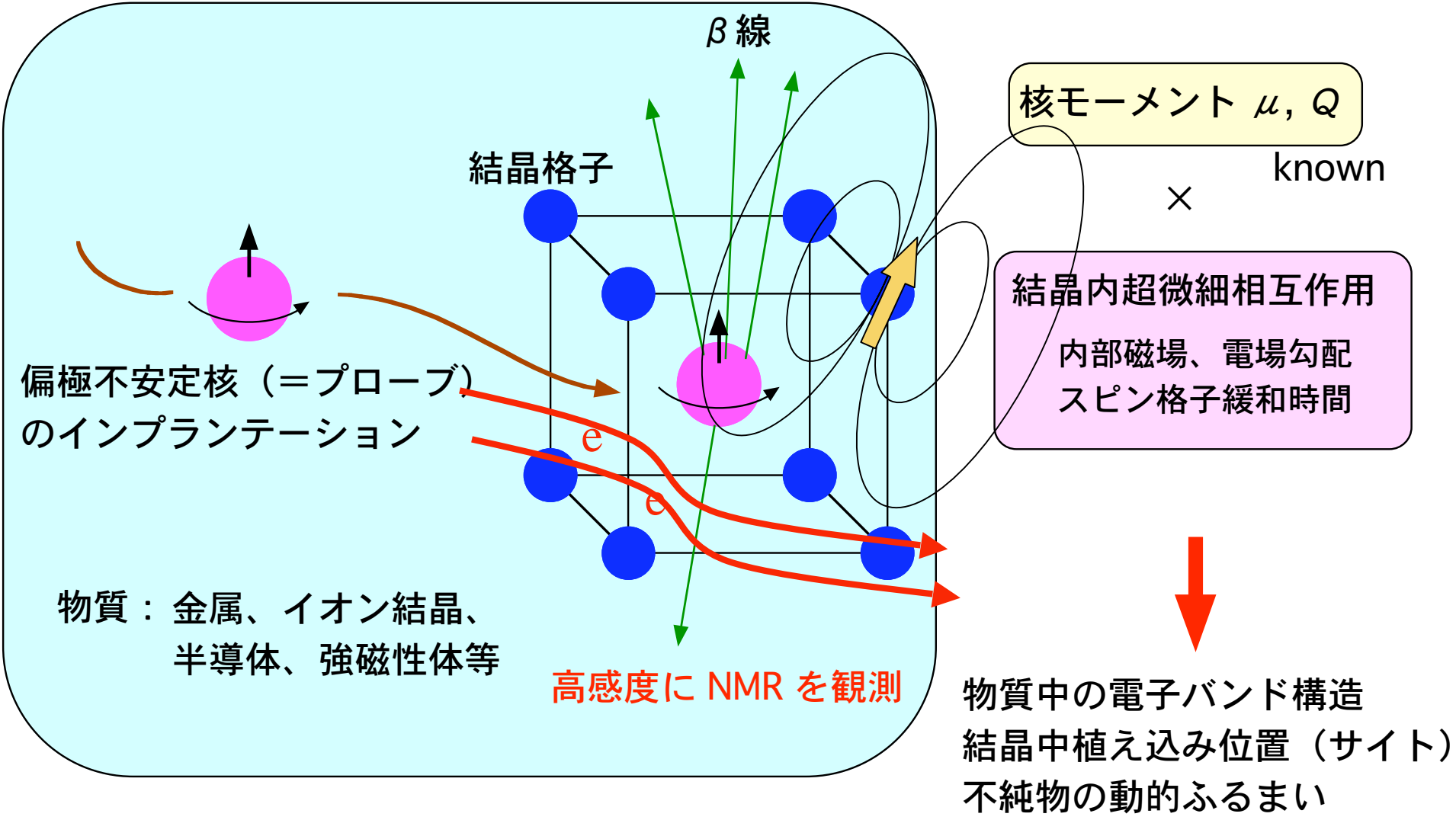
阪大理 松多健策、三原基嗣

阪大バンデグループ、HIMAC、理研、新潟大、高知工科大など

- β -NMR について
偏極不安定核の生成
実験原理、方法
- トピックス
金属中不純物のナイトシフト、 T_1
強磁性体中の超微細磁場
TiO₂ 中不純物の電場勾配、動的挙動
Si 中 ¹²B の動的挙動
金属中不純物のサイト
Na アイソトープの超微細相互作用

三原

β -NMR 法を用いた物性研究



β -NMRの時間スケール: 1 ms ~ 100 s, c.f. ns ~ μ s for PAC

Polarization in low energy nuclear reactions

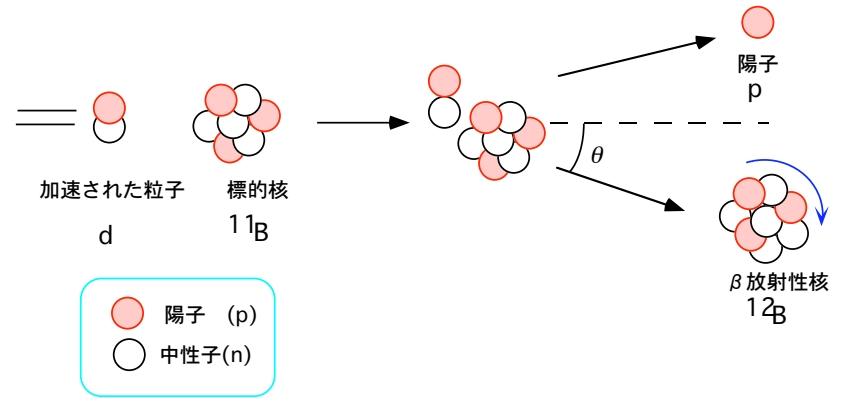
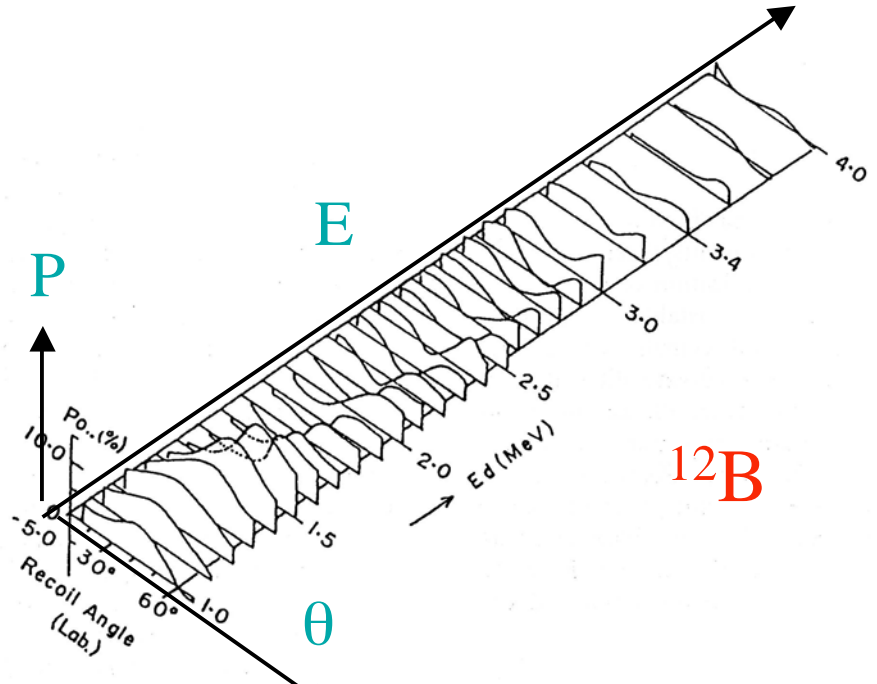
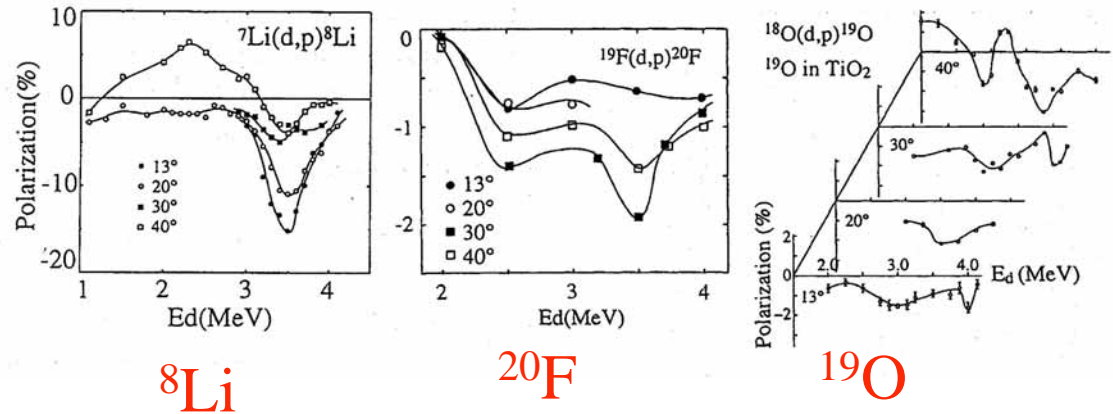
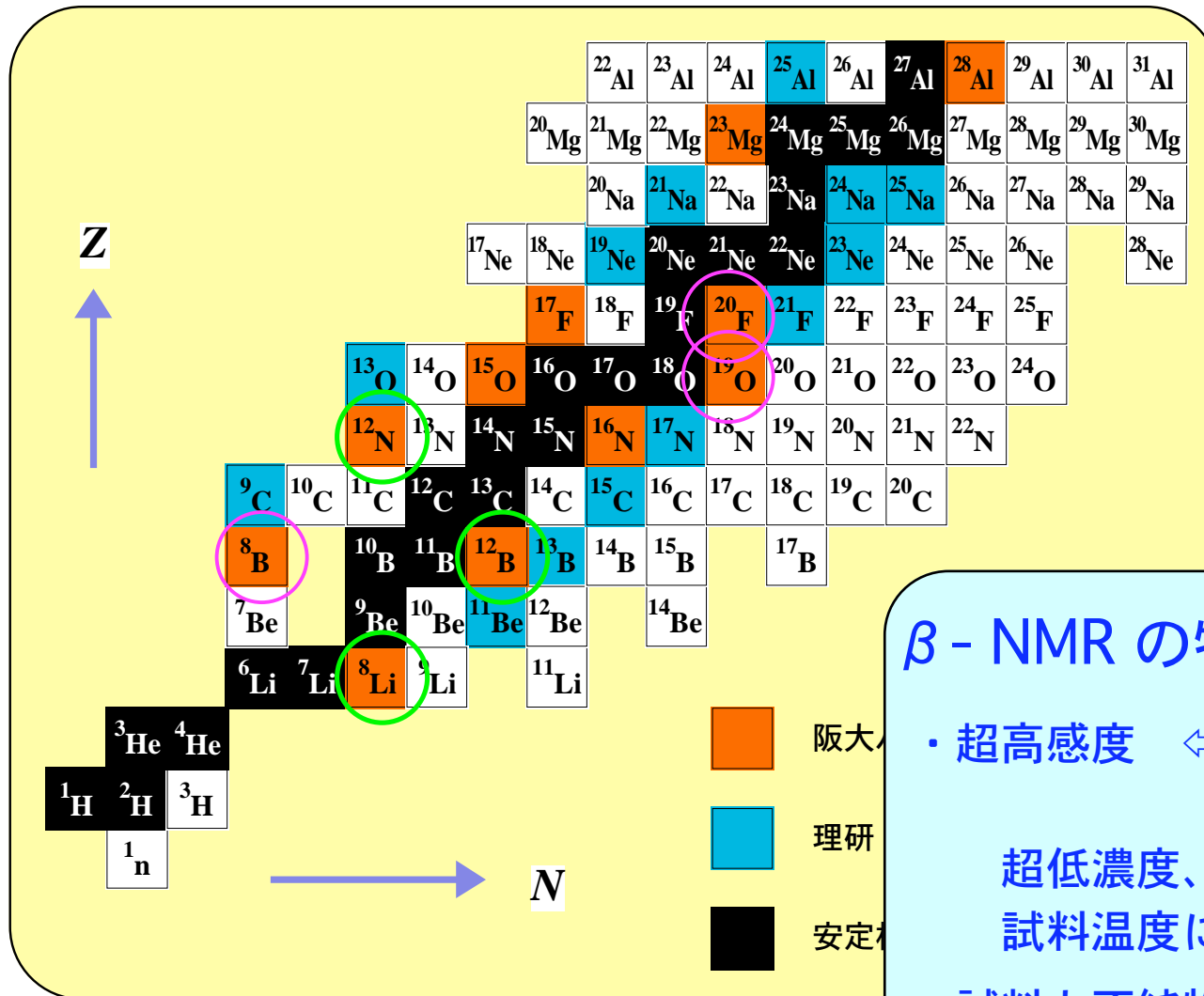


Fig. 1. Polarization of ^{12}B in the $^{11}\text{B}(d,p)^{12}\text{B}$ reaction. (This figure was taken from Ref. [3].)



Osaka
Hahn Meitner Institute
CIAE

偏極不安定核プローブ



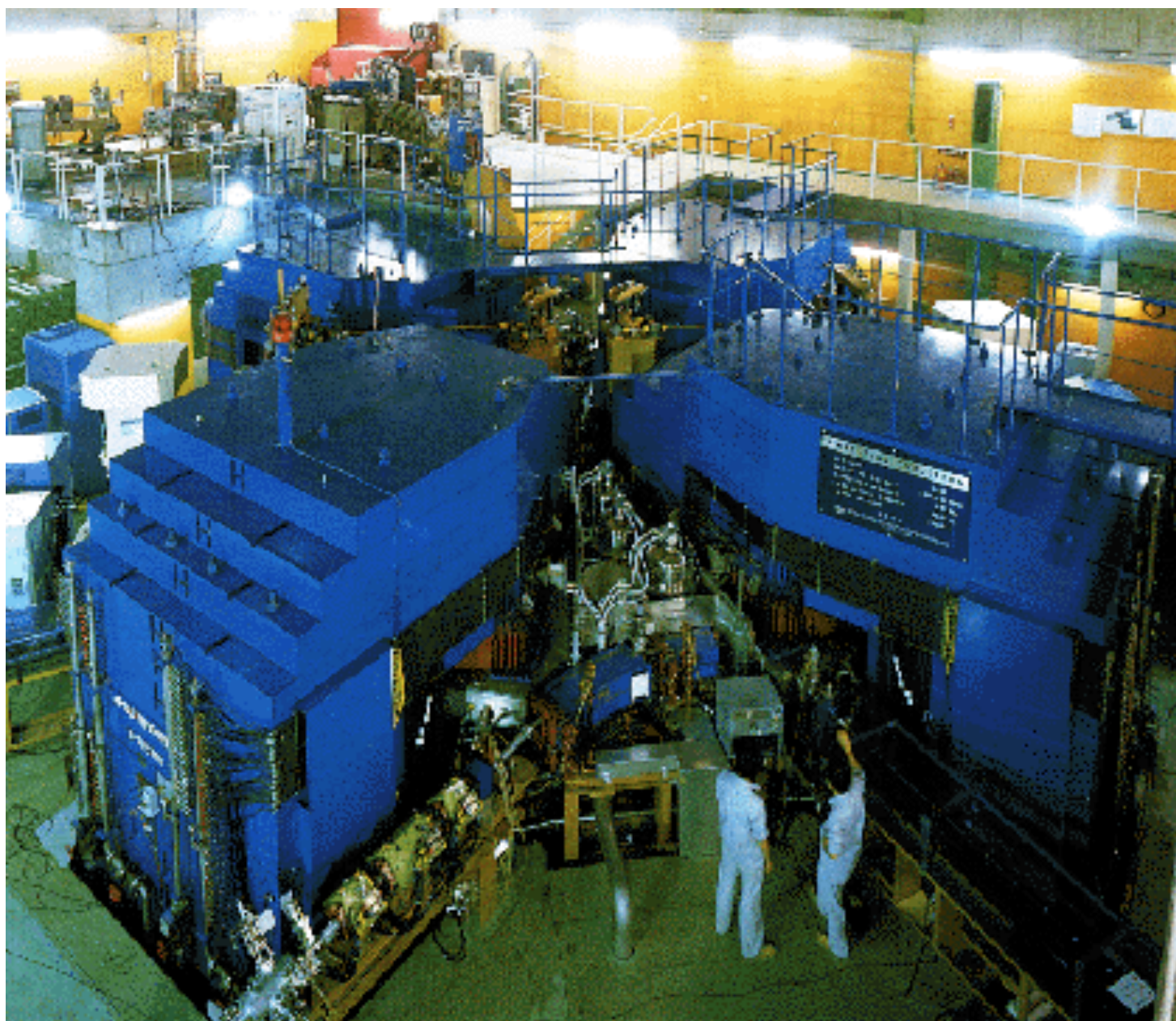
β - NMR の特徴

- ・ 超高感度 $\leftarrow \beta$ 線検出
核反応による高偏極
超低濃度、不純物間の相互作用がない
試料温度によらない (10 - 1000 K)
- ・ 試料と不純物の組み合わせが自由
- ・ スピン格子緩和時間 T_1
 \geq プローブ核の寿命
(10 ms ~ 100 s)

Osaka 5MV Van de Graaff

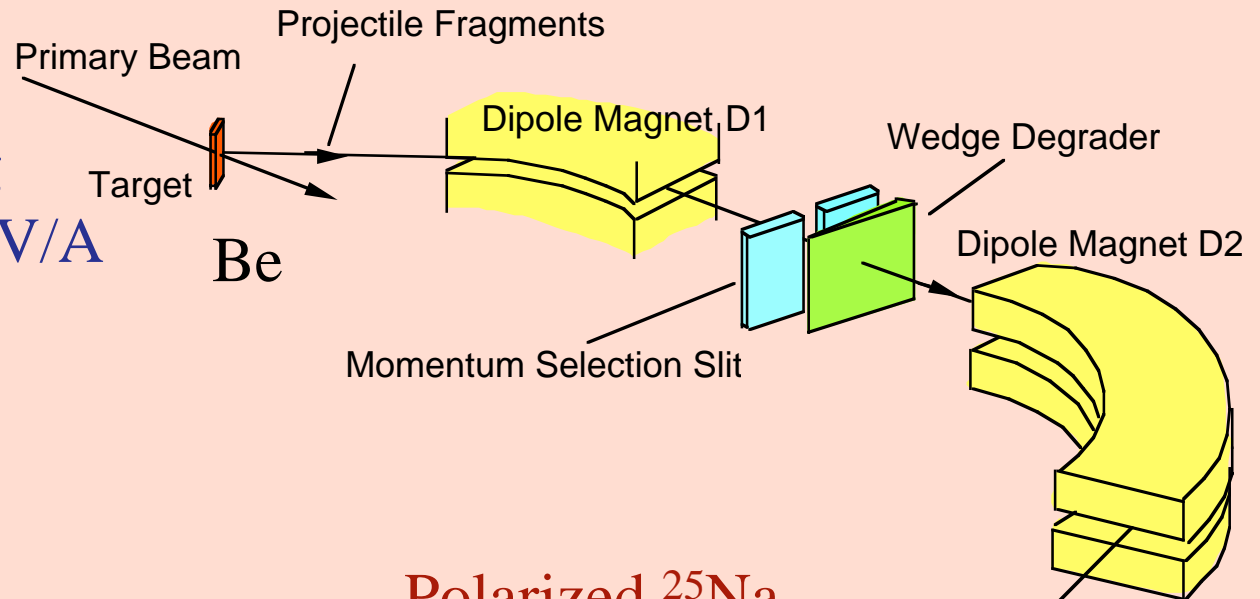


理化学研究所

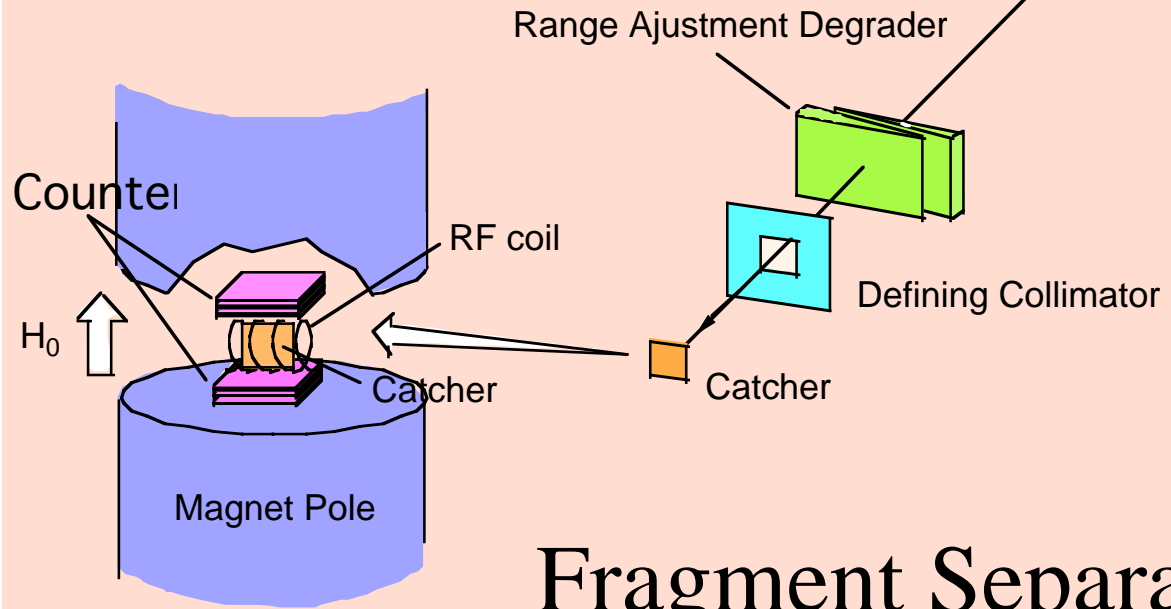


HIMAC

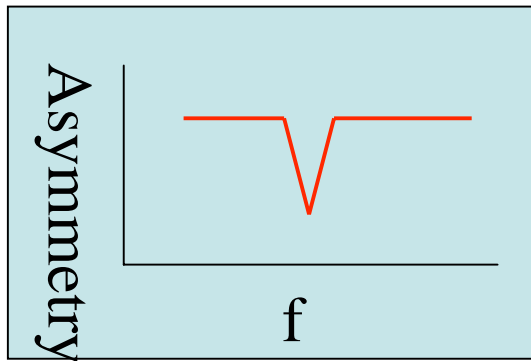
^{26}Mg
100 MeV/A



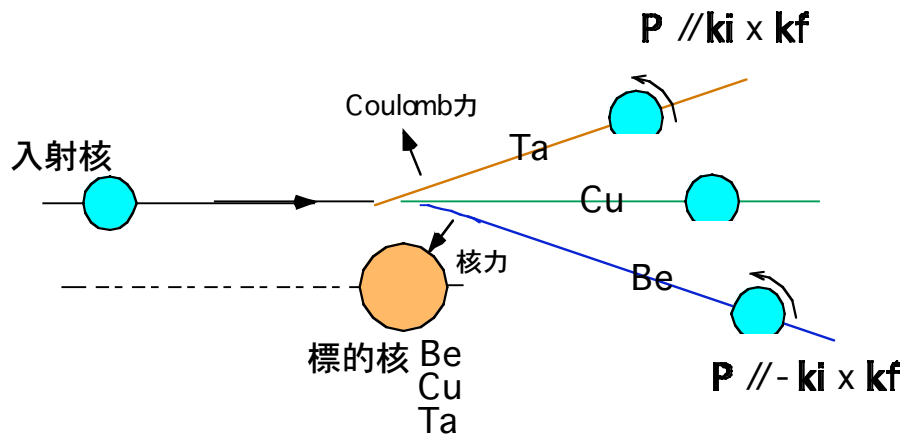
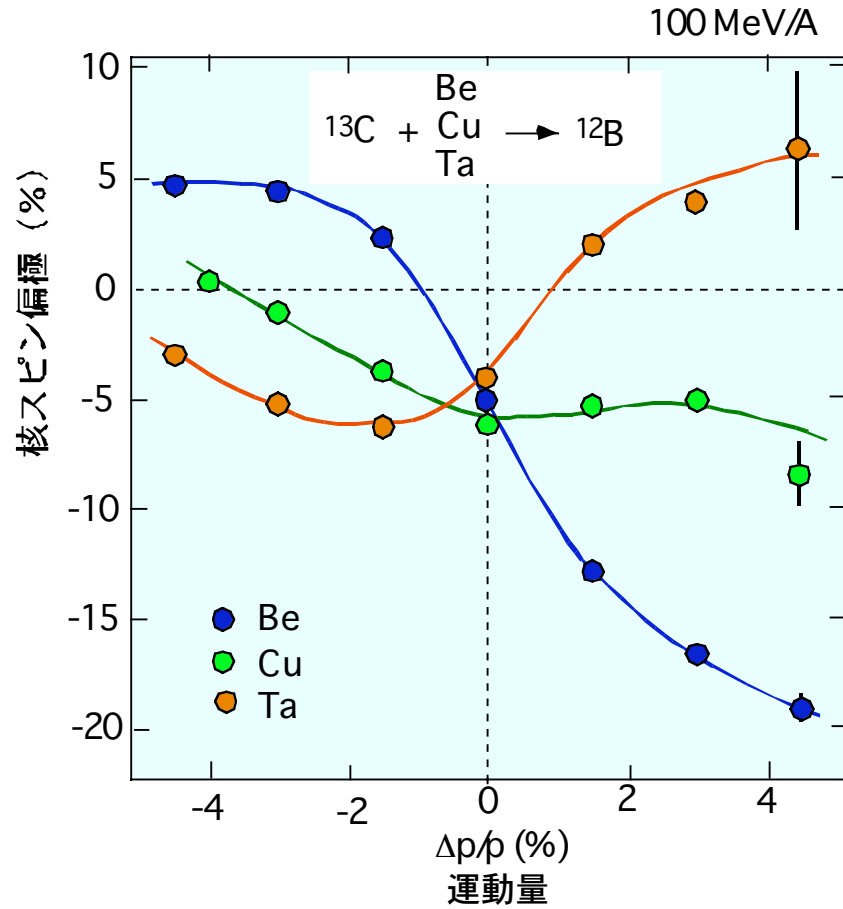
Polarized ^{25}Na



Fragment Separator

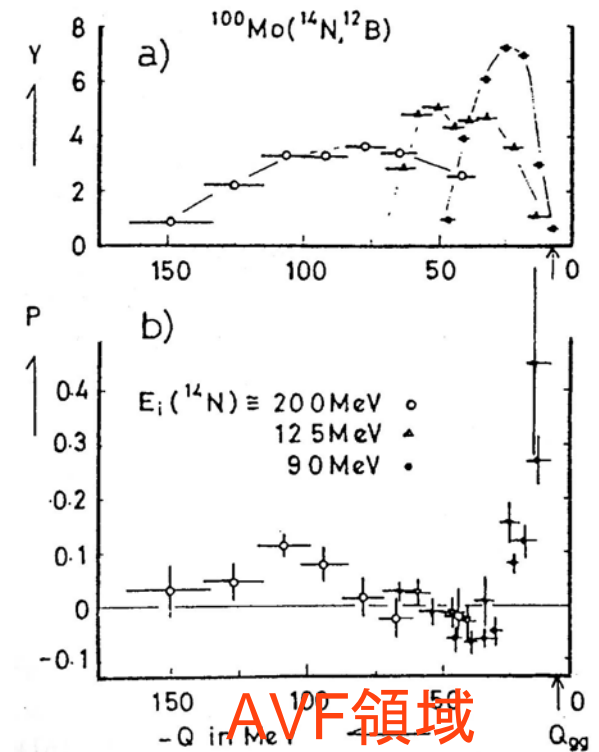


高エネルギー入射核破碎過程での偏極機構

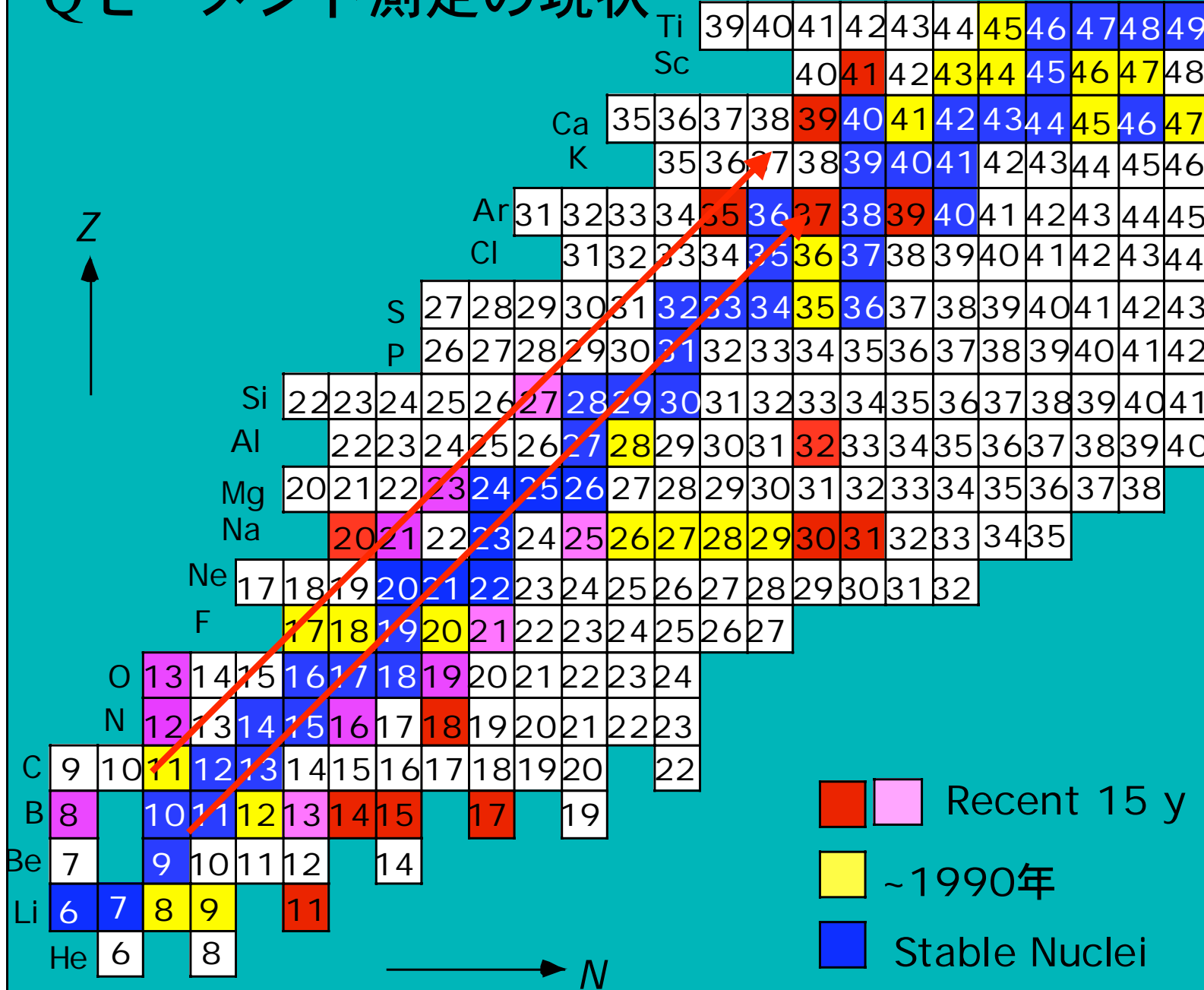


理研 RIBF;
戻しビームライン

阪大 RCNP;
ビーム強度増大化



Qモーメント測定の実況

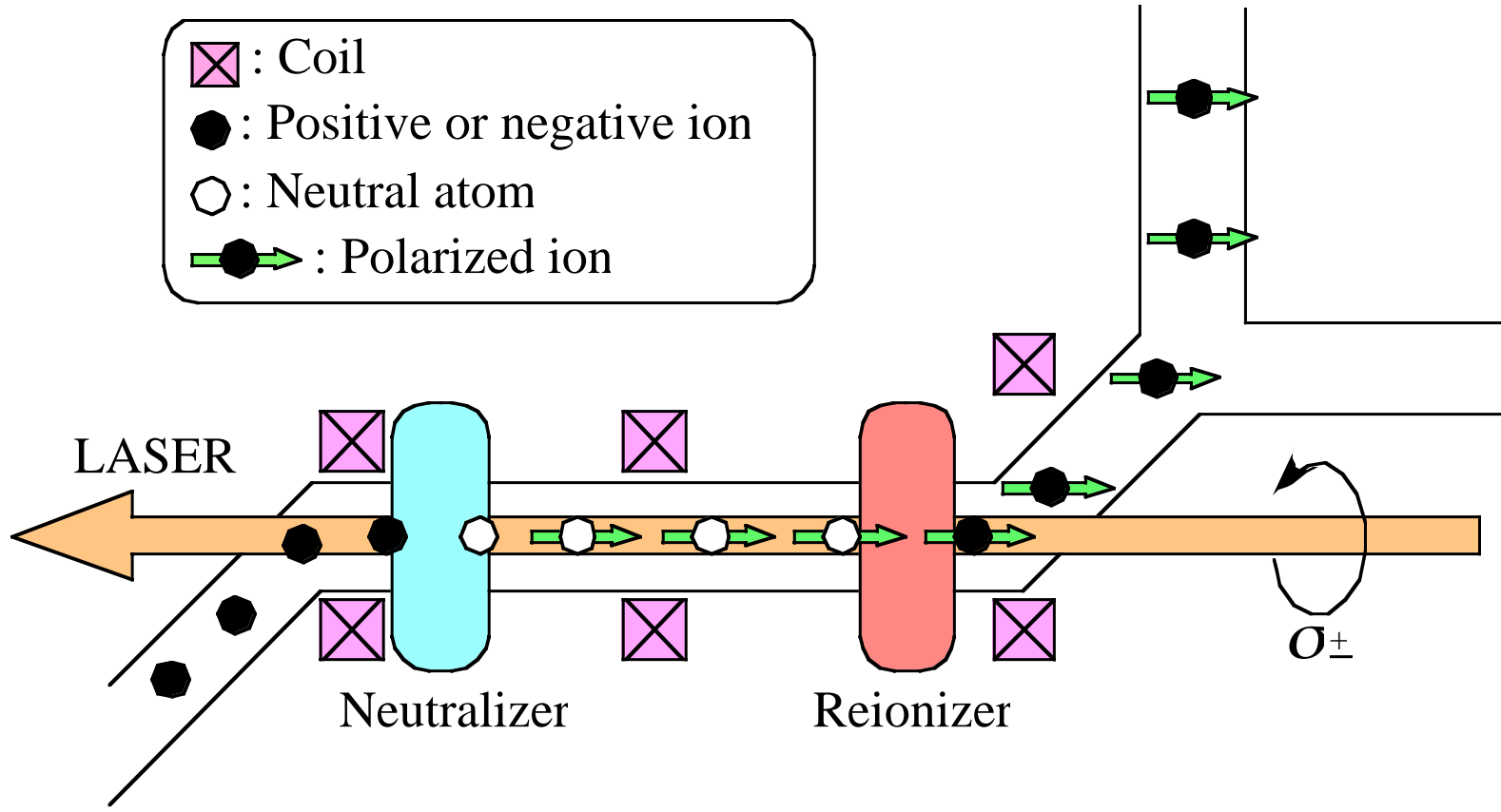


Polarizer beam line

TRIUMF/ISAC Polarizer Beamline

OSAKA II
Exp. port

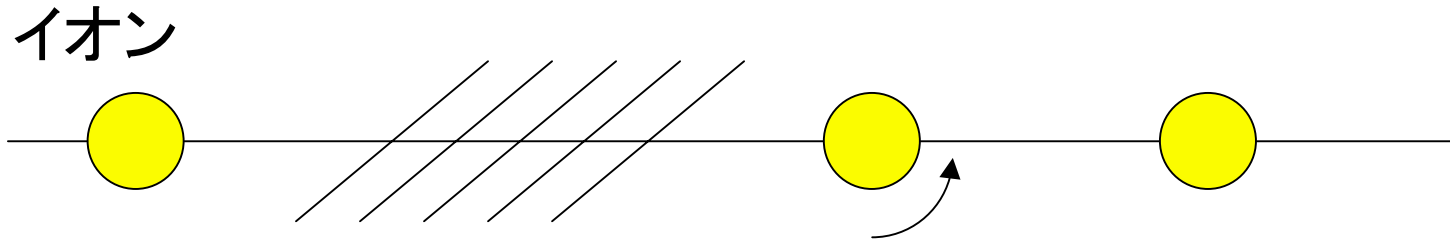
- ⊠ : Coil
- : Positive or negative ion
- : Neutral atom
- ➡ : Polarized ion



傾斜薄膜法

ISOLに適している

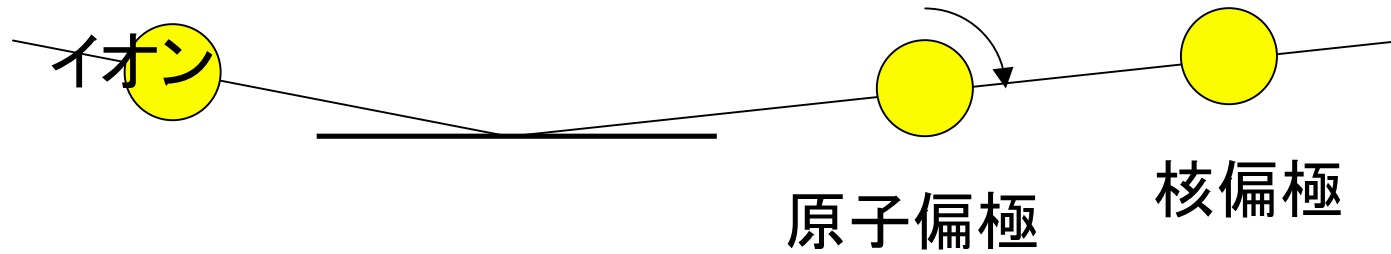
原研TRIAC



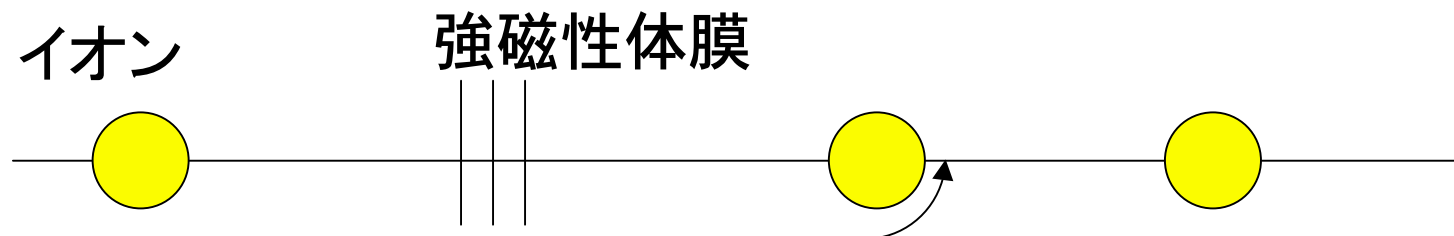
原子偏極 → 核偏極

超微細相互作用

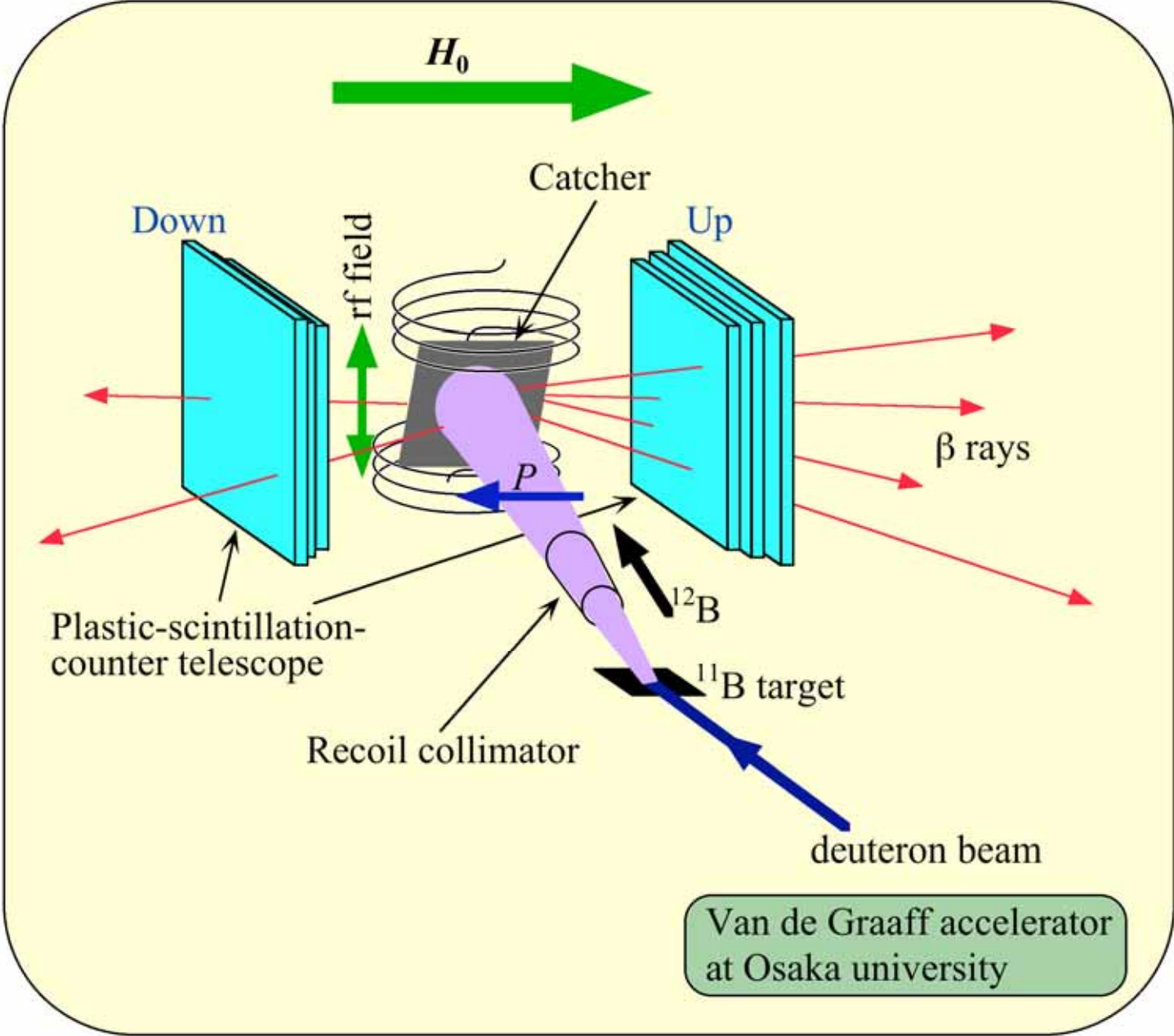
微小角散乱法

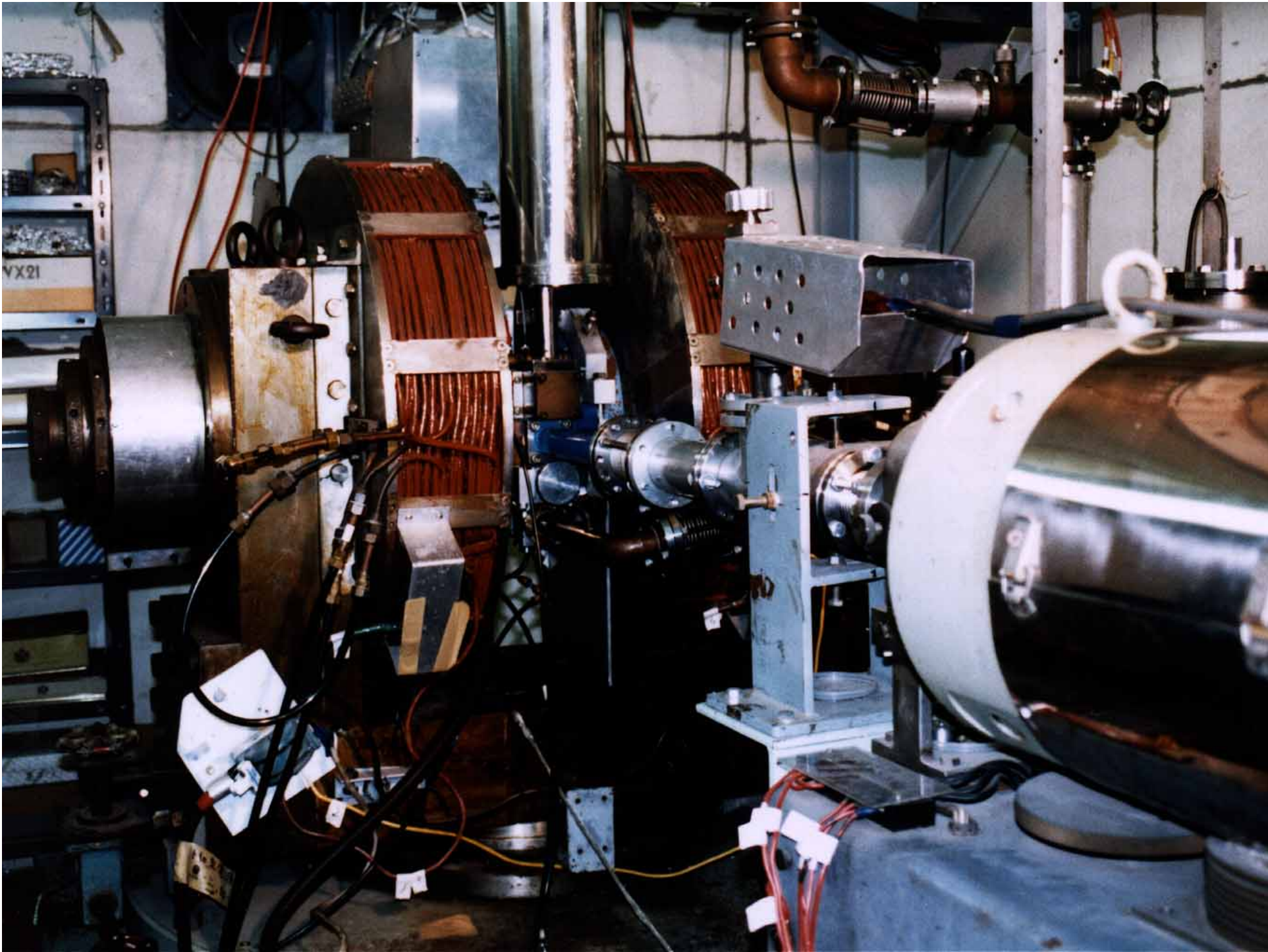


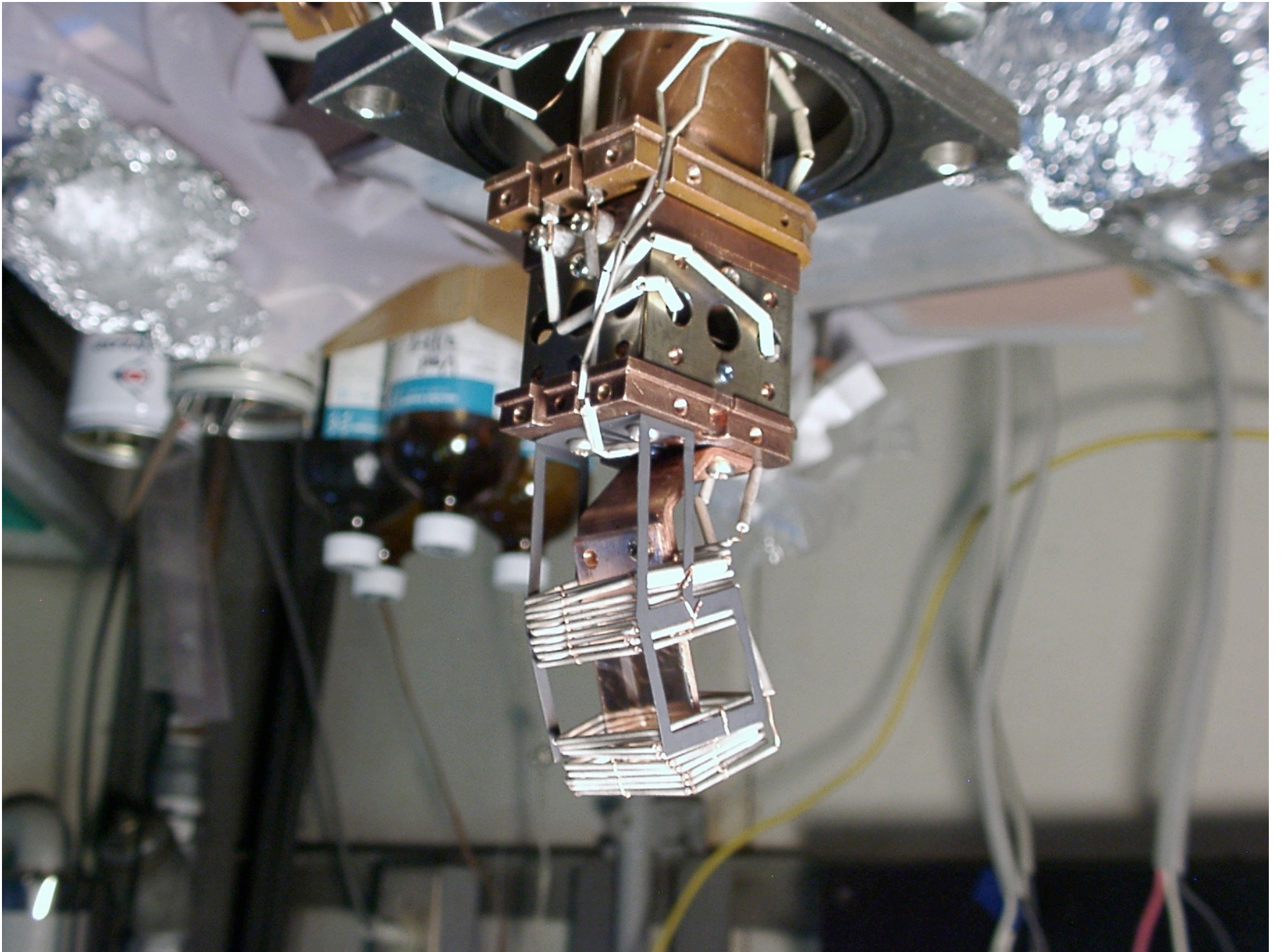
トランジェントフィールド



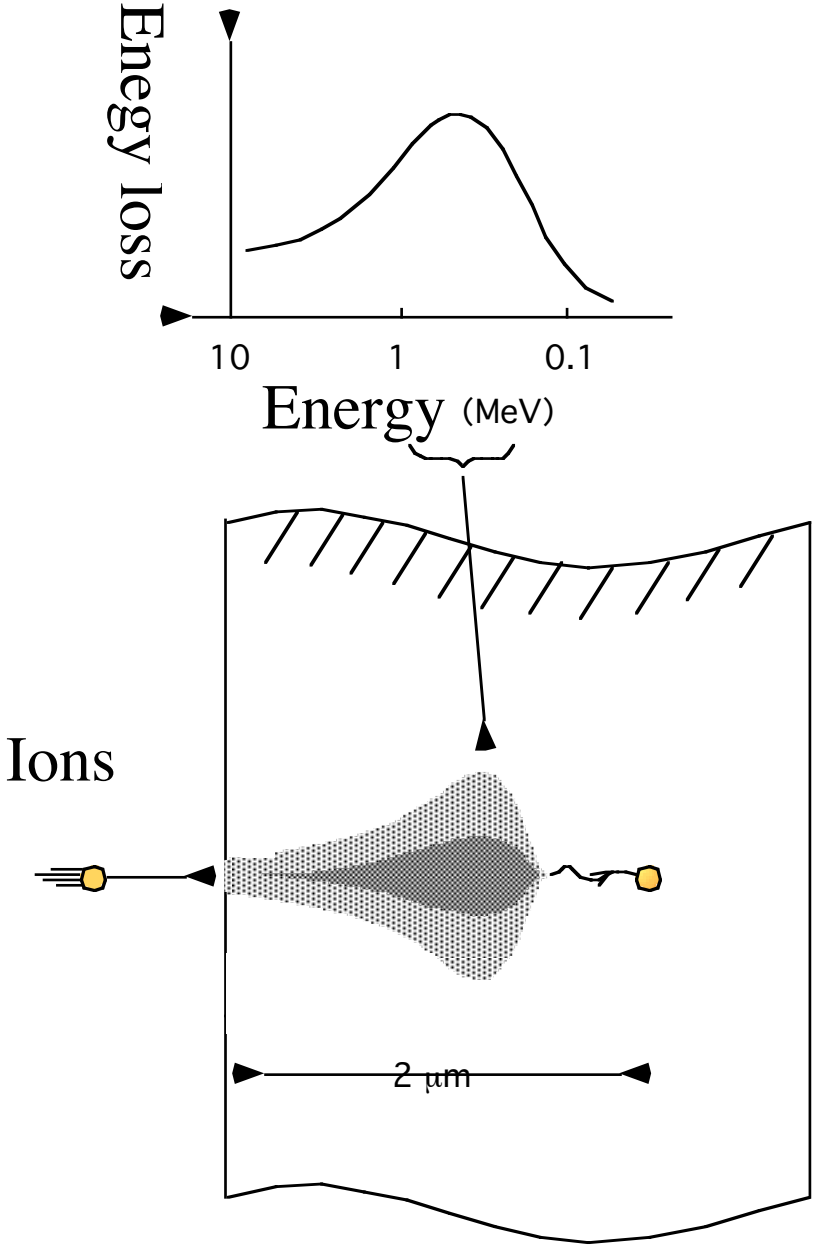
Setup (阪大 VdG)



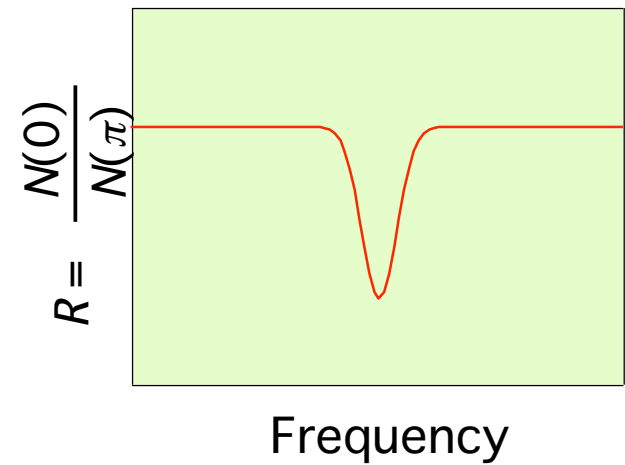
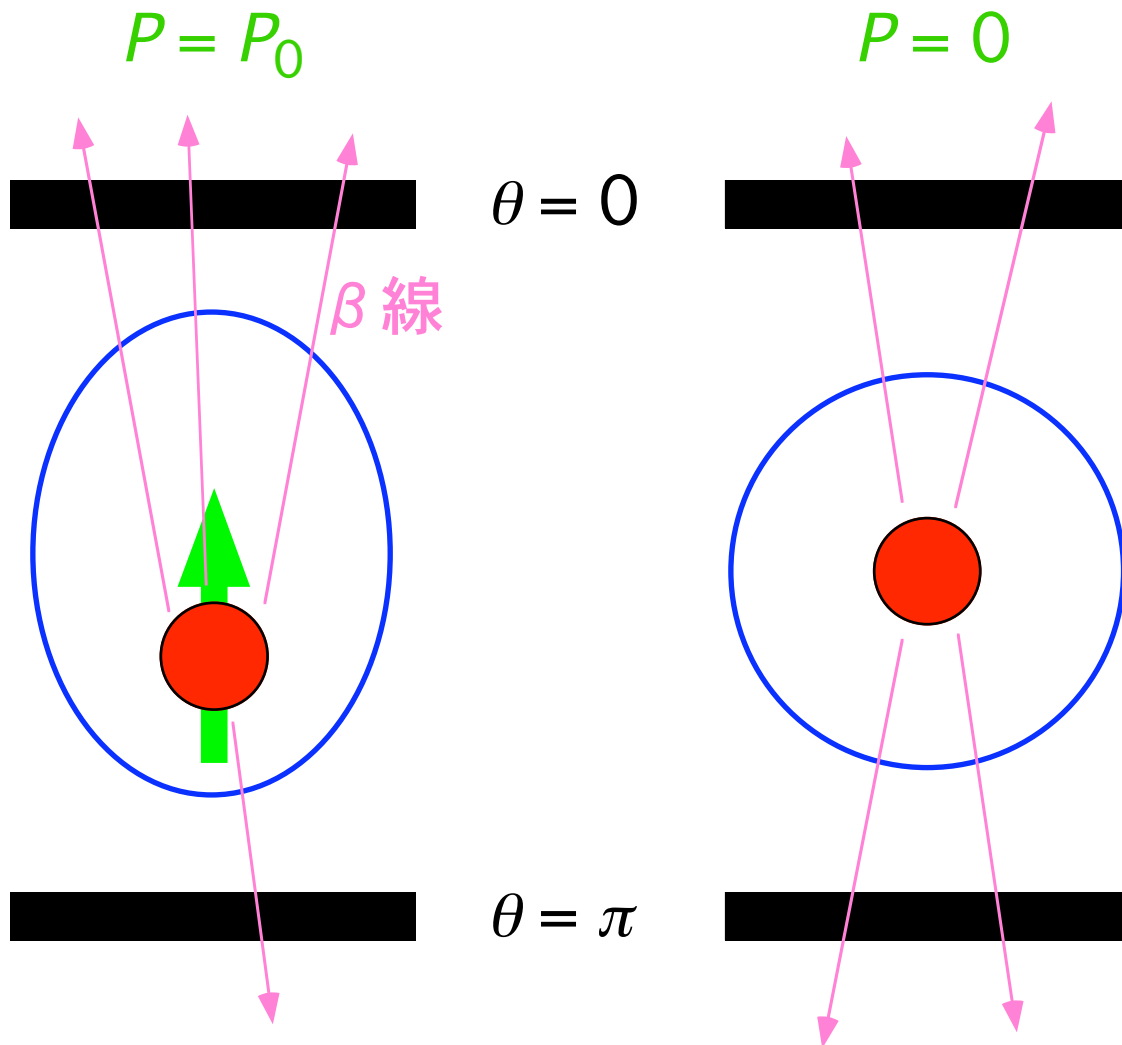




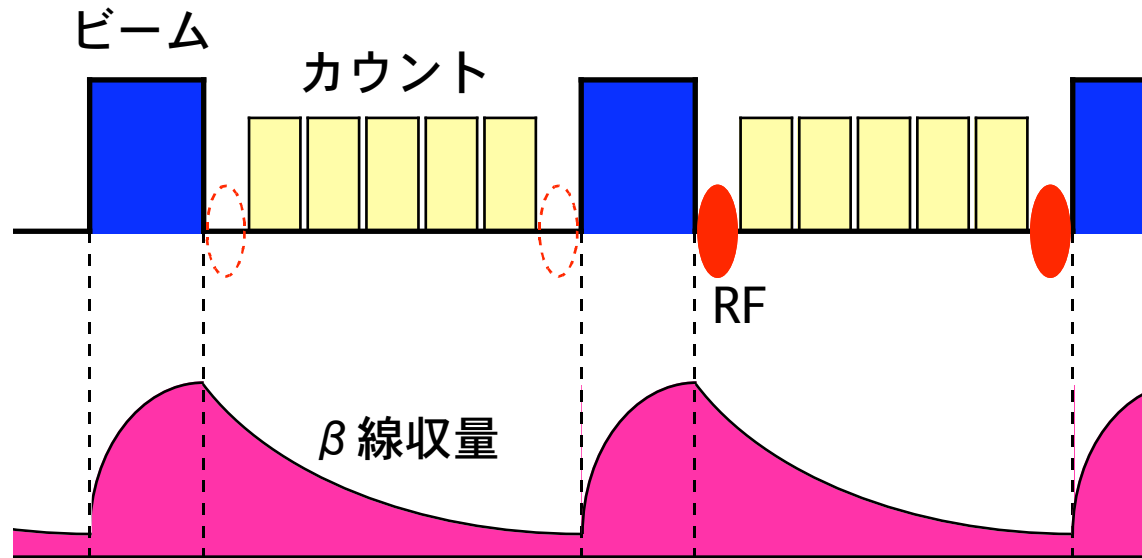
Implantation



β 線角度分布： $W(\theta) = 1 + AP \cos\theta$



タイムシーケンス



偏極

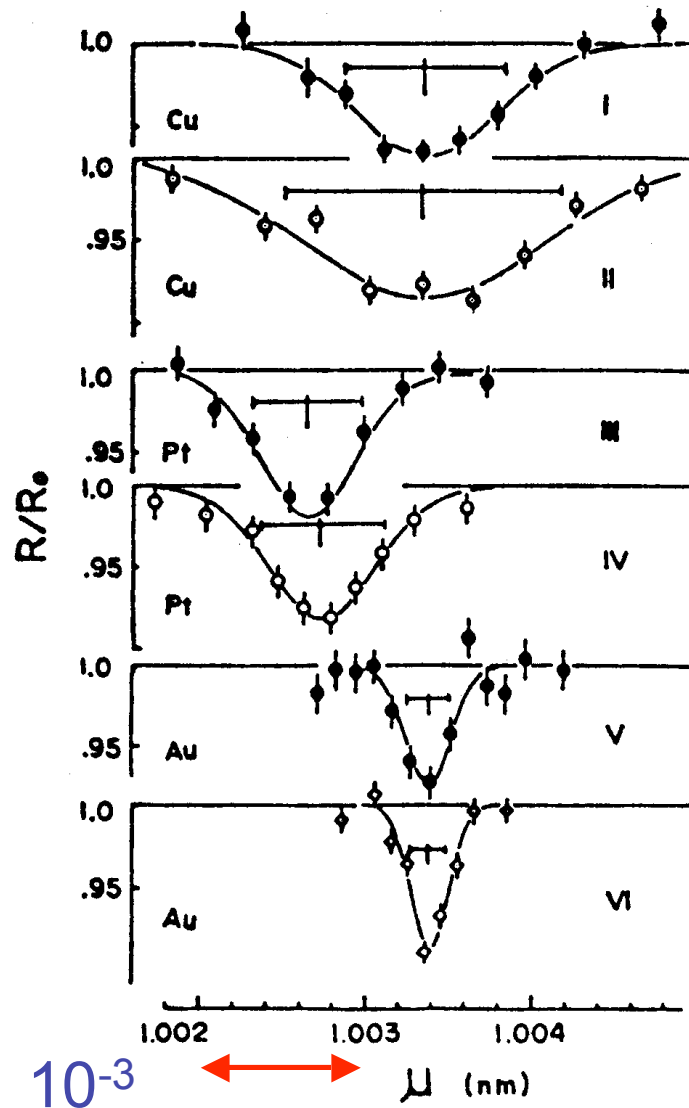


$$\Delta AP = \frac{\sqrt{R} - 1}{\sqrt{R} + 1}$$

$$\left(R = \frac{N(0)}{N(\pi)} \right)$$

金属中の電子バンド構造

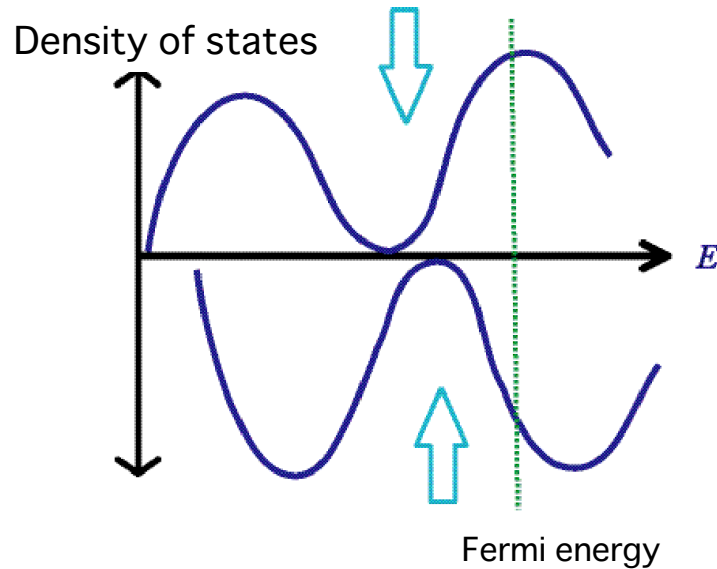
----- NMR スペクトルのシフト -----



NMR spectra
 ^{12}B in various metals

ナイトシフト : K

金属結晶中不純物のナイトシフト



原子核位置での電子状態密度を反映する。

第一原理計算との比較によりバンド構造の詳細を明らかにする。

ナイトシフト： K

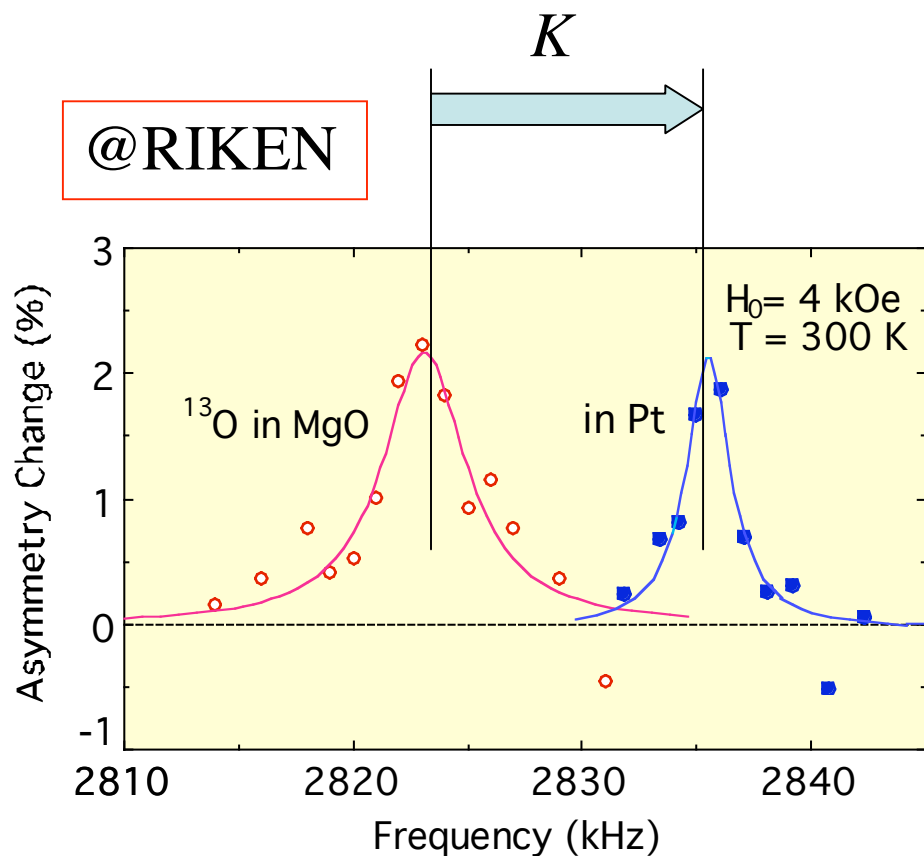
$$K = \frac{\Delta H}{H_0} = \frac{8\pi}{3} \mu_B^2 \int^{E_F} \left\{ \rho_{\uparrow}(0, E) - \rho_{\downarrow}(0, E) \right\} dE / H_0$$

スピン格子緩和時間： T_1

$$(T_1 T)^{-1} = (8/9) h k_B \gamma_n^2 \gamma_e^2 \rho_{\uparrow}(0, E_F) \rho_{\downarrow}(0, E_F)$$

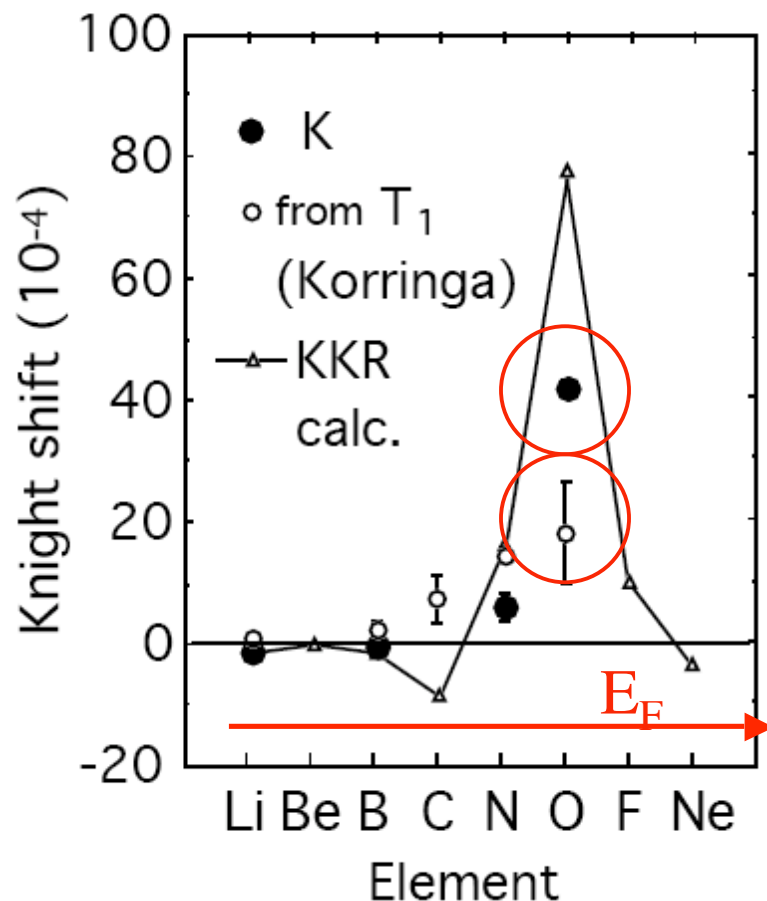
コリンハの関係： $(T_1 T) K^2 = \text{一定}$

Pt 中不純物のナイトシフト K

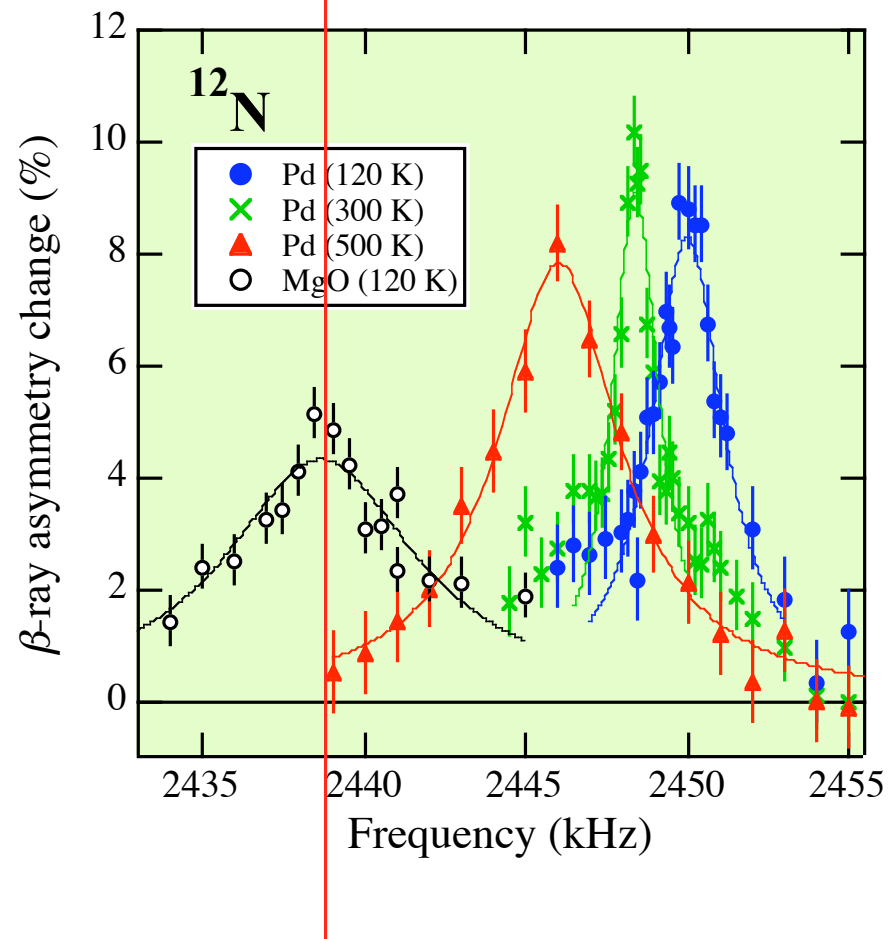
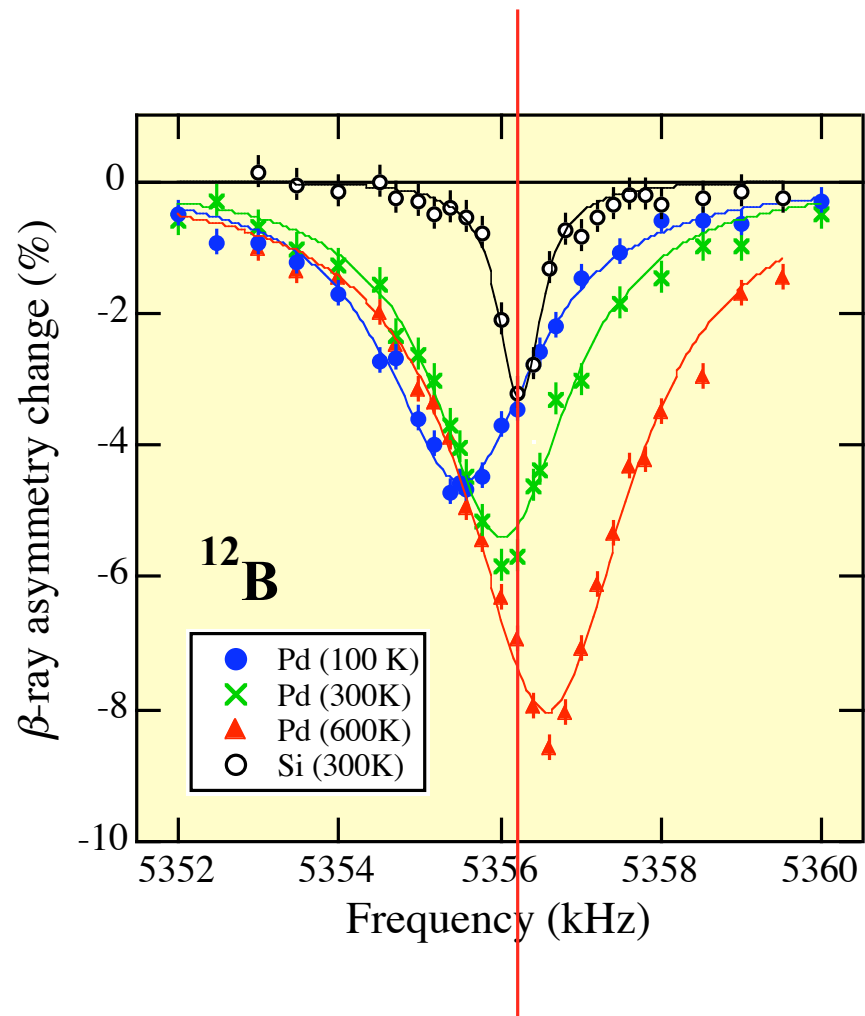


$$K = \Delta H / H_0 = \mu_B^2 \int^{E_F} \{ \rho_{\uparrow}(0, E) - \rho_{\downarrow}(0, E) \} dE / H_0$$

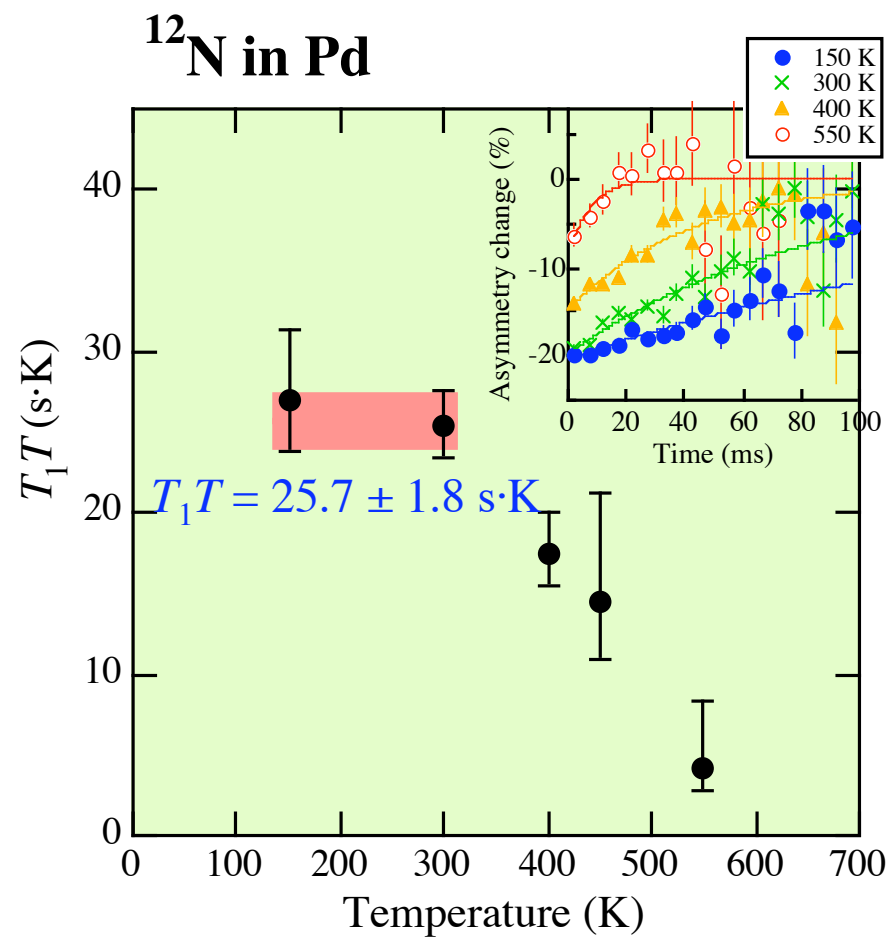
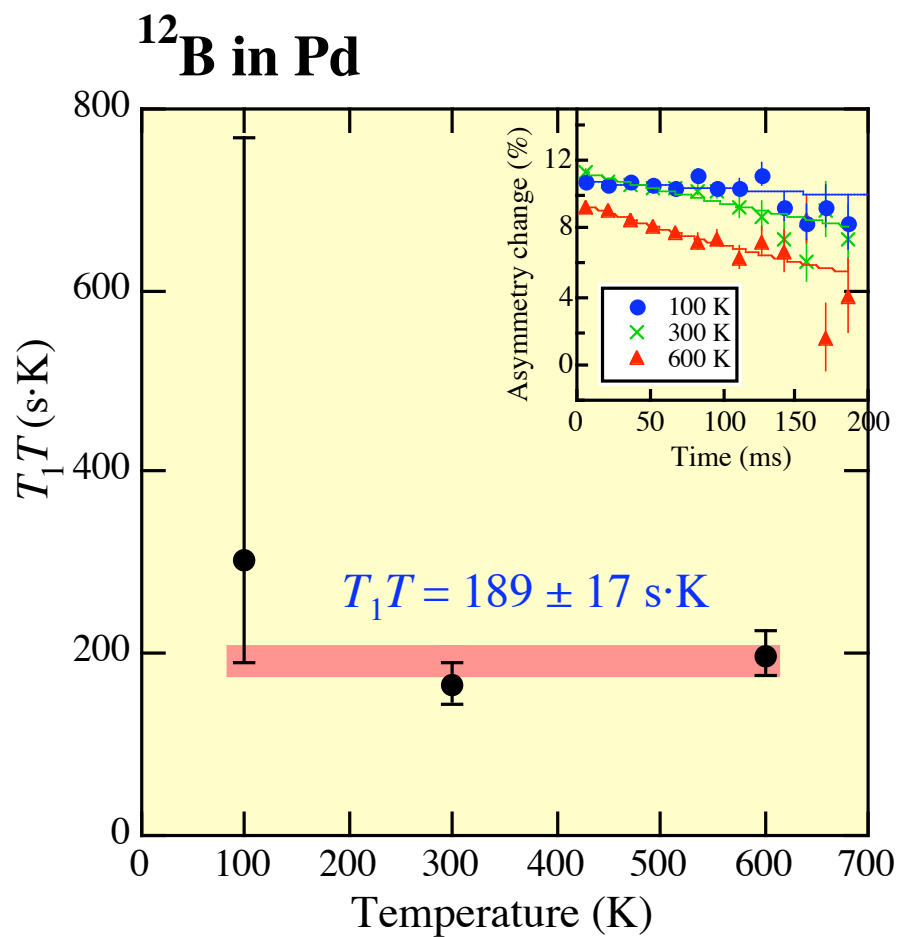
$$(T_1 T)^{-1} = (8/9) h k_B \gamma_n^2 \gamma_e^2 \rho_{\uparrow}(0, E_F) \rho_{\downarrow}(0, E_F)$$



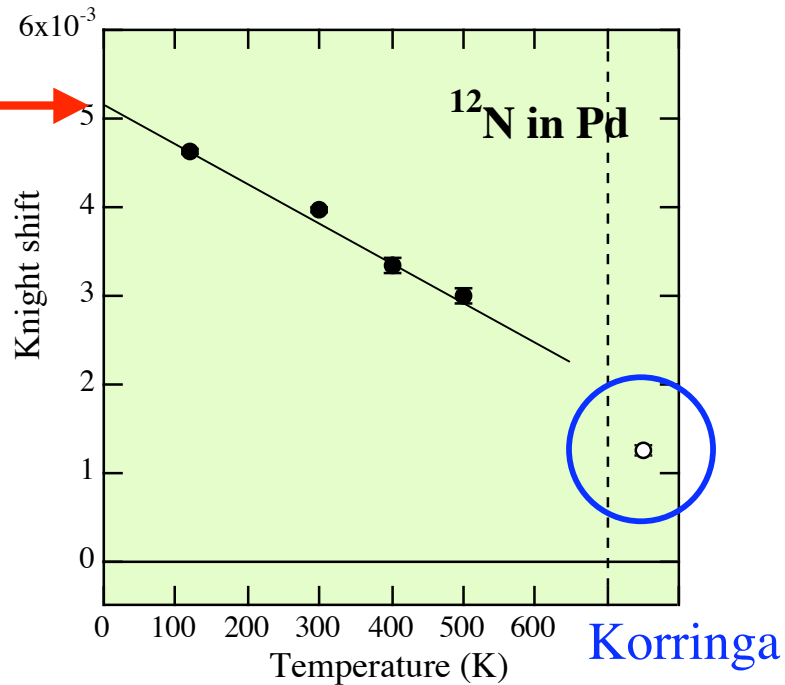
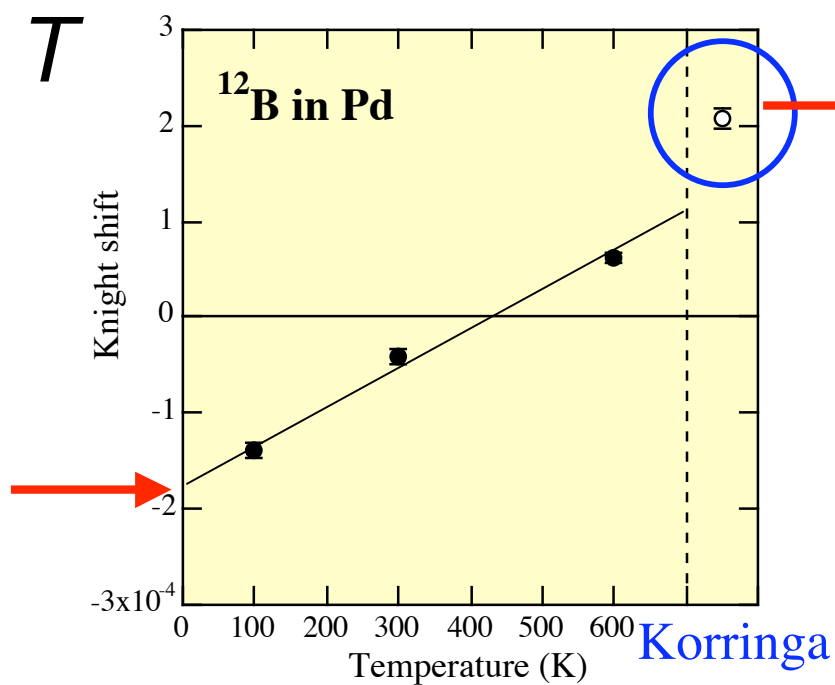
Pd 中 ^{12}B , ^{12}N のナイトシフト



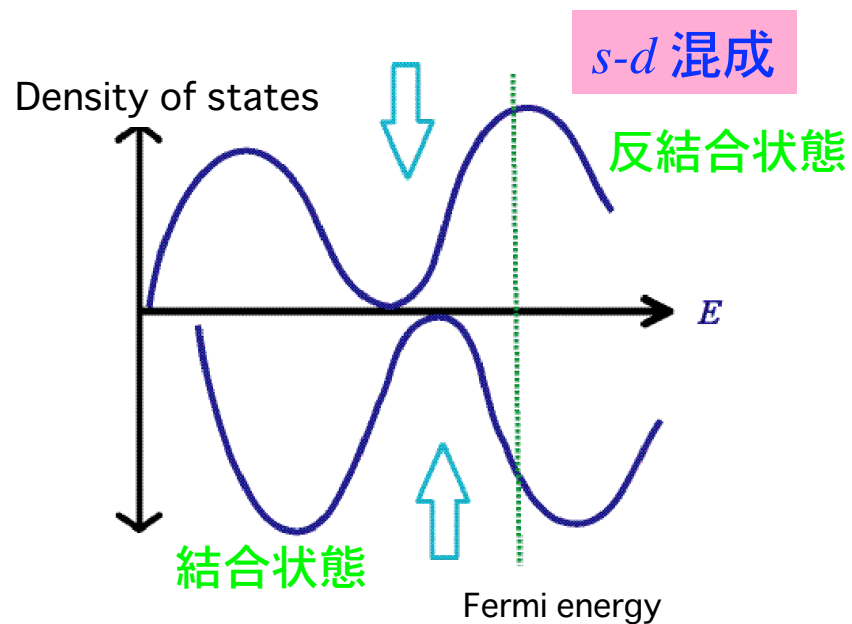
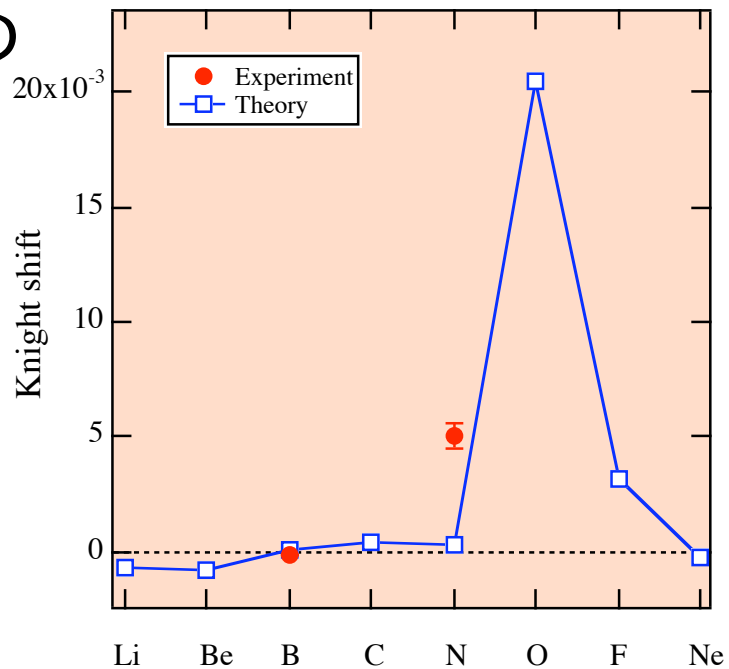
Pd 中 ^{12}B , ^{12}N のスピン格子緩和時間



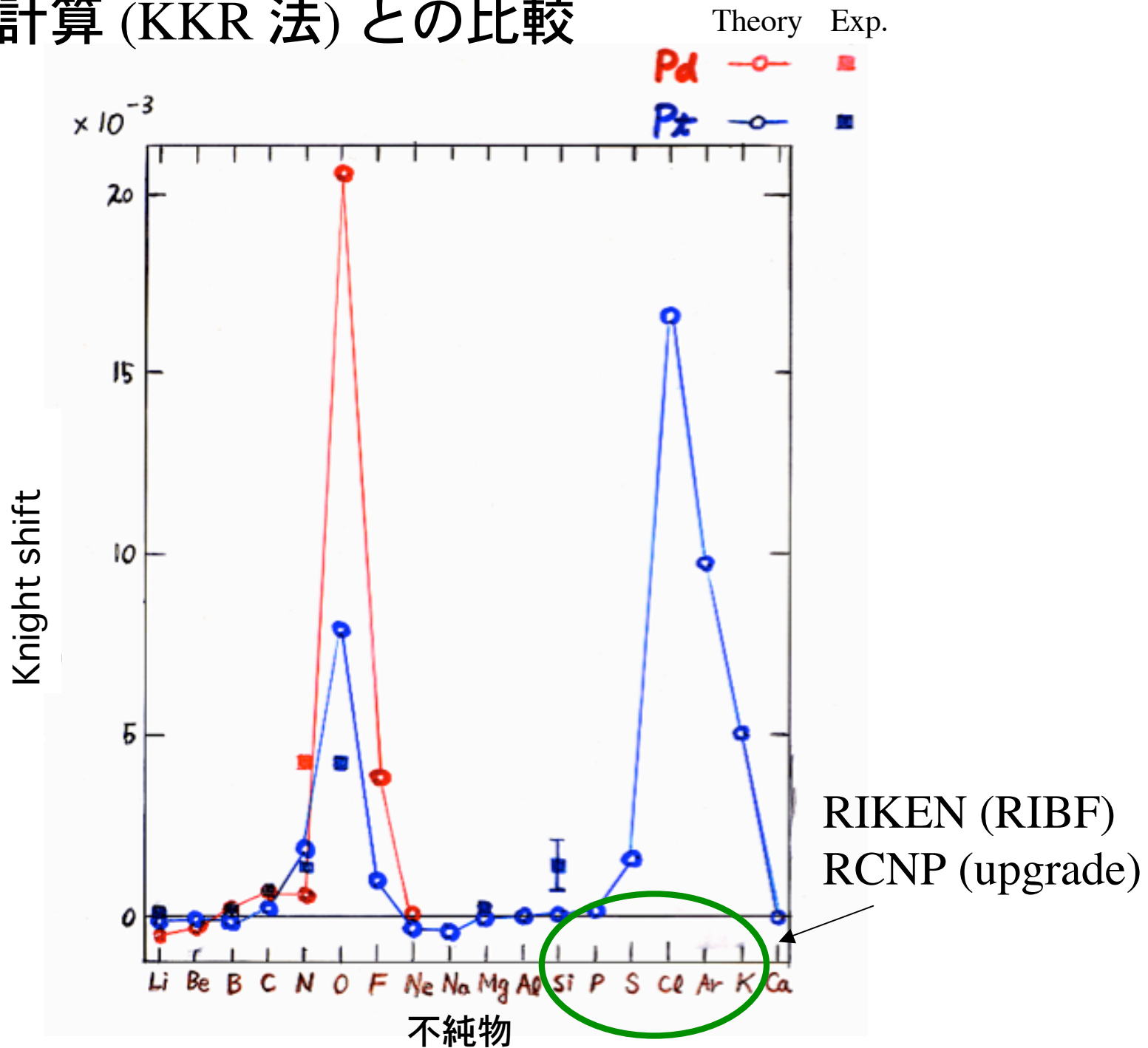
K vs T



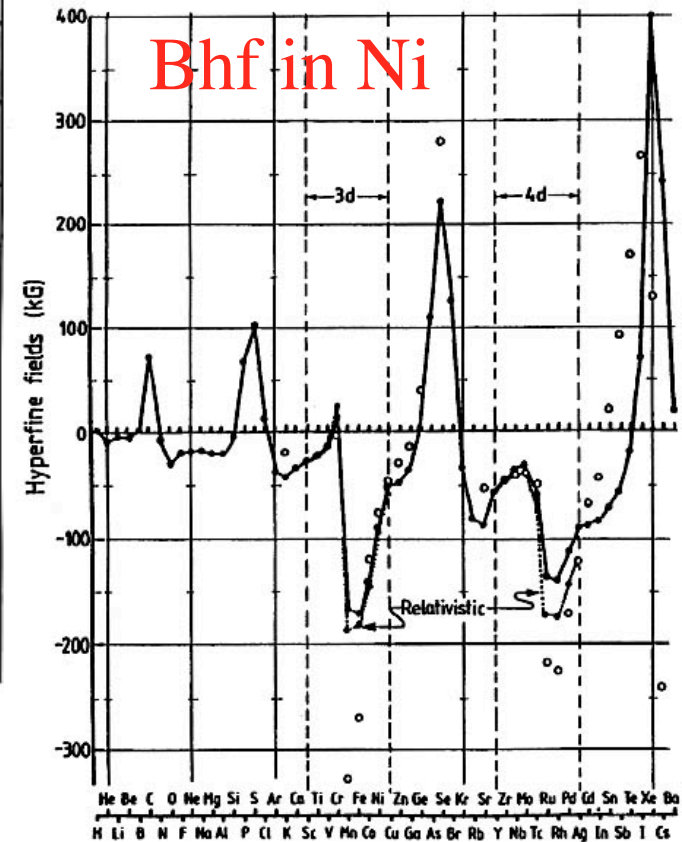
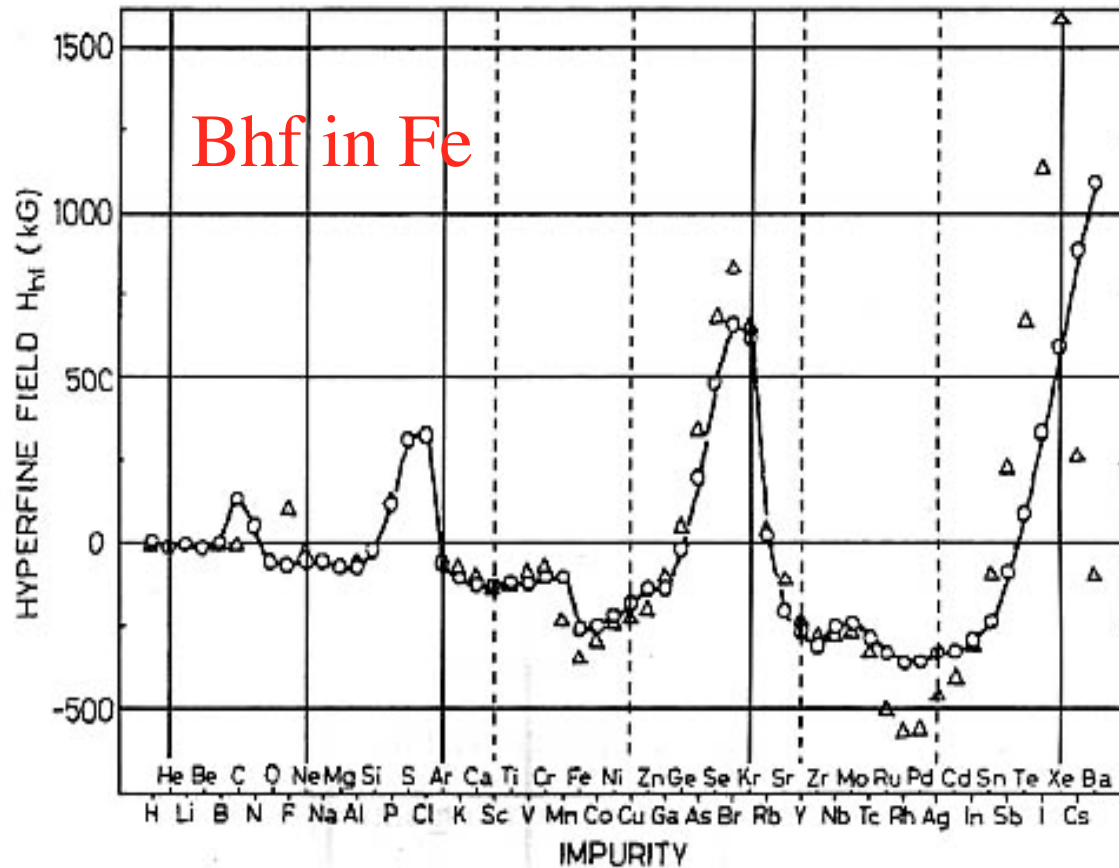
計算との比較



第一原理計算 (KKR 法) との比較



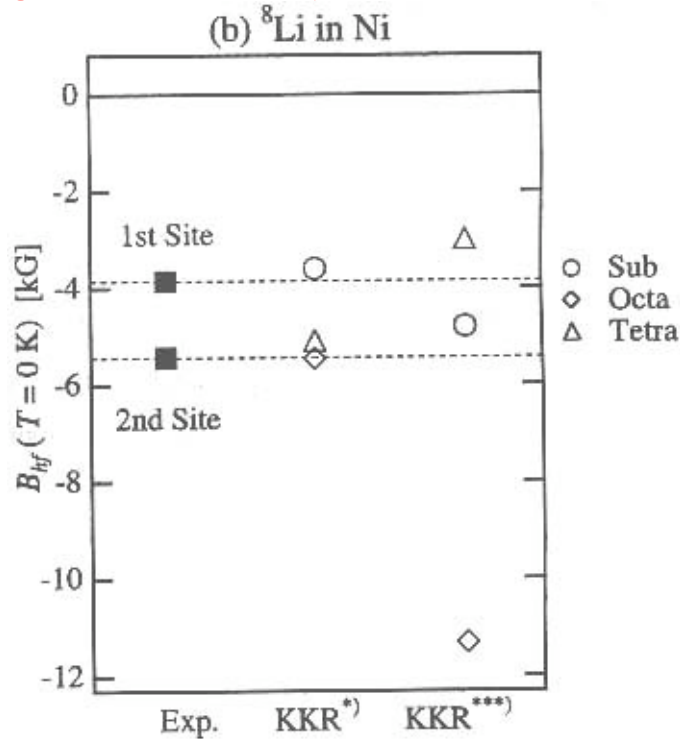
強磁性体中の超微細磁場



$$H_{hf} = \mu_B^2 \int^{EF} \{ \rho_{\uparrow}(0, E) - \rho_{\downarrow}(0, E) \} dE$$

$$(T_1 T)^{-1} = (8/9) h k_B \gamma_n^2 \gamma_e^2 \rho_{\uparrow}(0, E_F) \rho_{\downarrow}(0, E_F)$$

B_{hf} for ^8Li in Ni



第2サイトは動きやすい
= 間隙位置

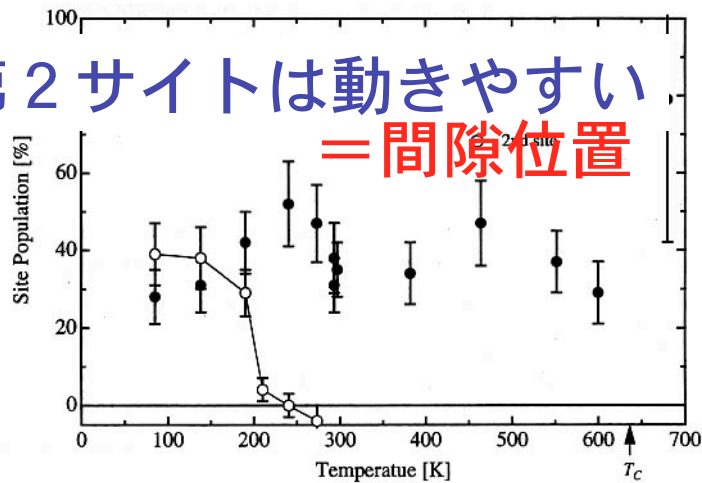


Fig.40 Temperature dependences of the site populations.

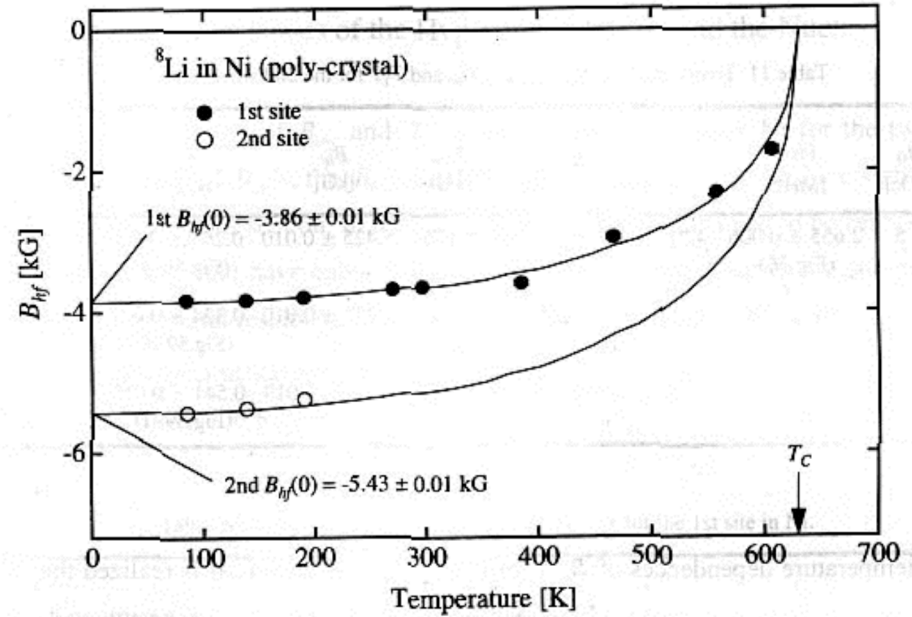


Fig.38 Temperature dependences of B_{hf} 's for ^8Li in Ni by the 8AP method. The solid lines are the best which are proportional to the bulk magnetization curves $M_s(T)$

2ヶ所に止まる

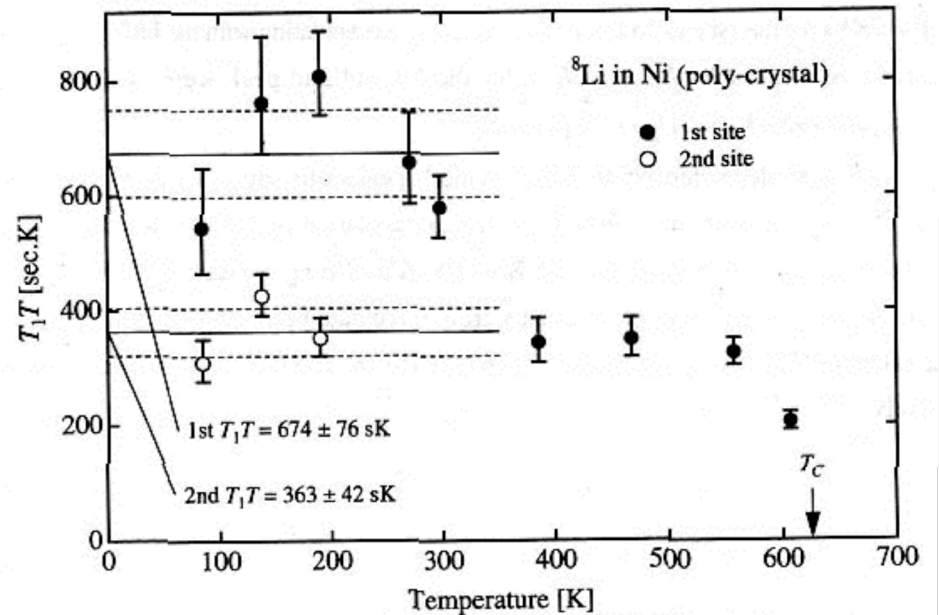


Fig.39 Temperature dependences of T_1T 's for ^8Li in Ni.

Nd₂Fe₁₄B (NEOMAX)

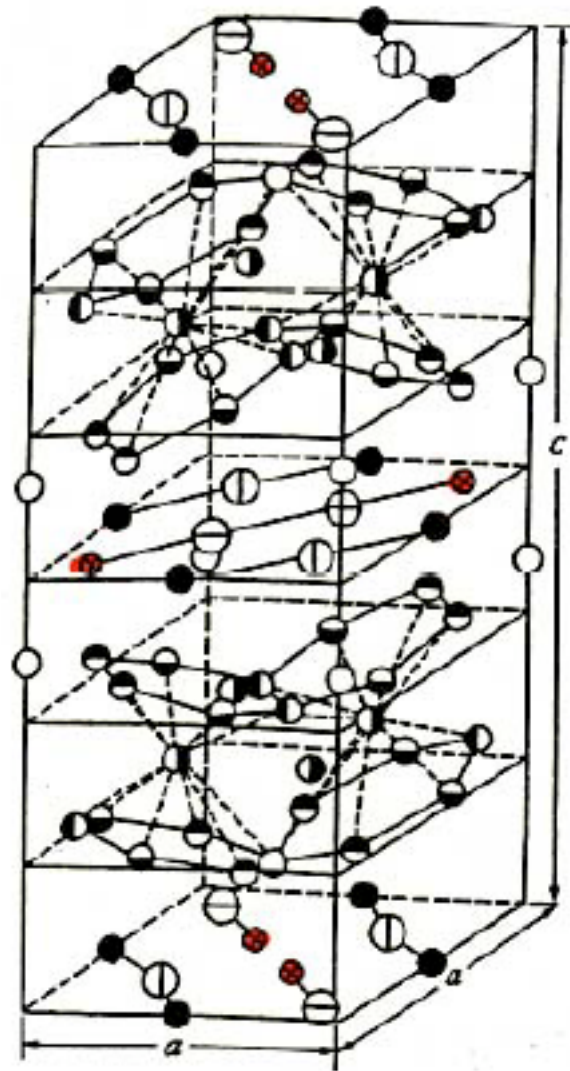
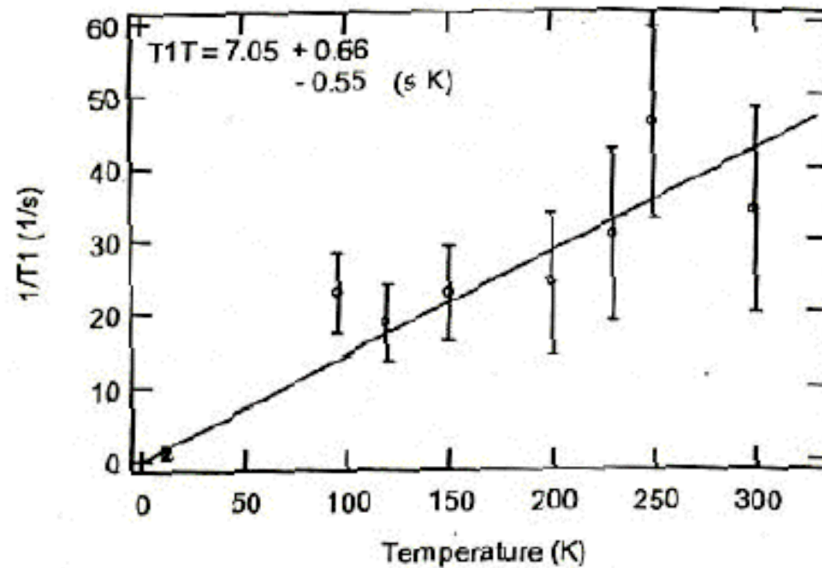
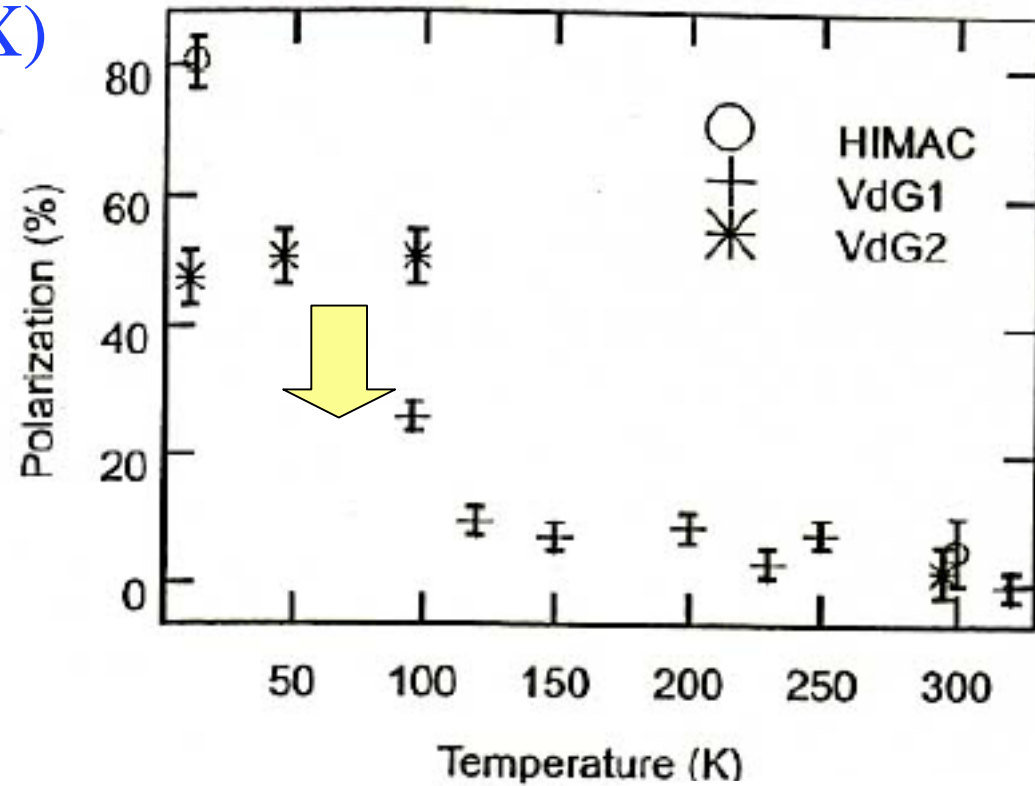


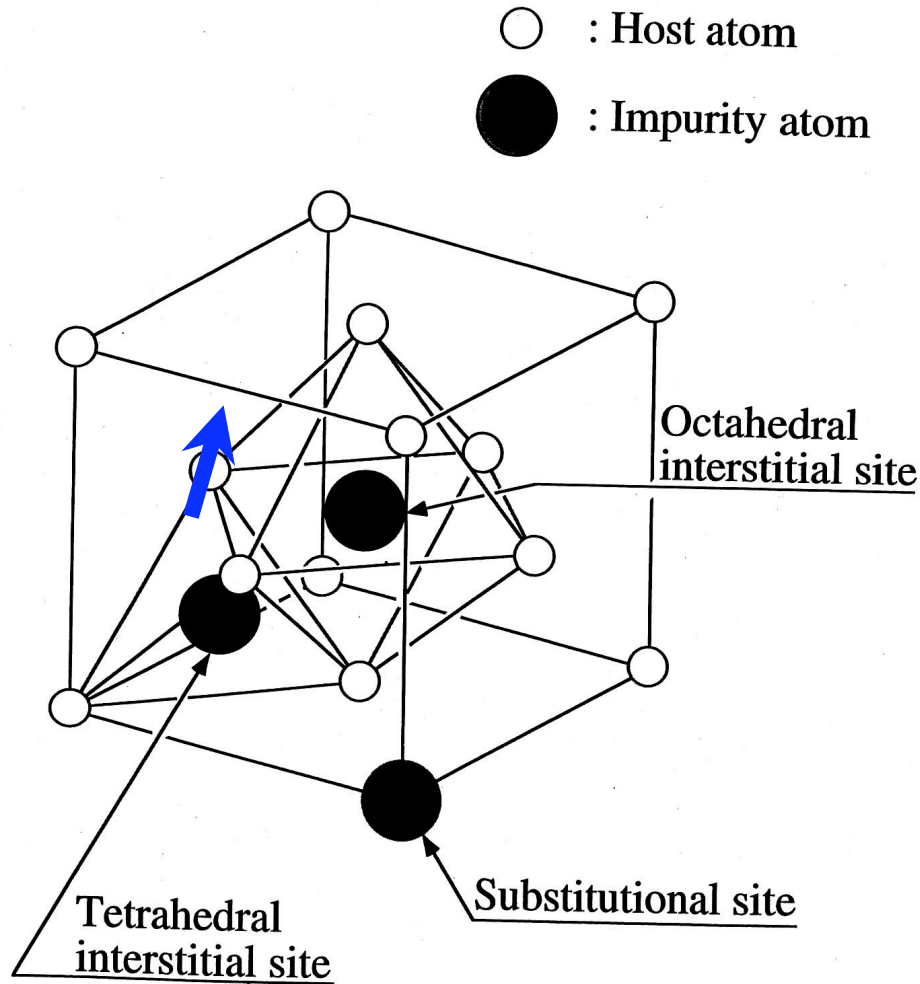
Fig. 1 R₂Fe₁₄Bの結晶構造²⁾

Fig.1 Polarizability
function of temperature
 ● Fe_{j2}
 ● Fe_{k1}
 ● Fe_{k2}
 ⊗ B_g



不純物サイト同定

双極子幅と結晶内のイオンのインプラネーション位置



ホスト核の磁気モーメント



双極子磁場

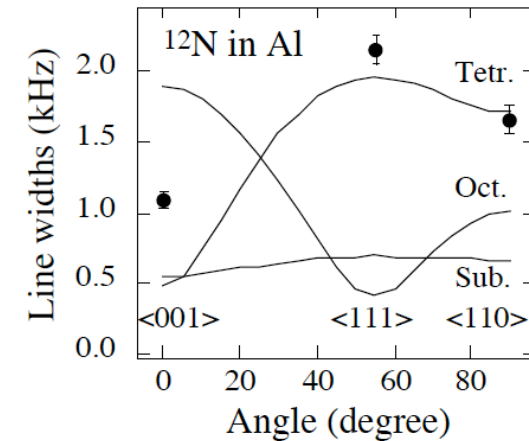
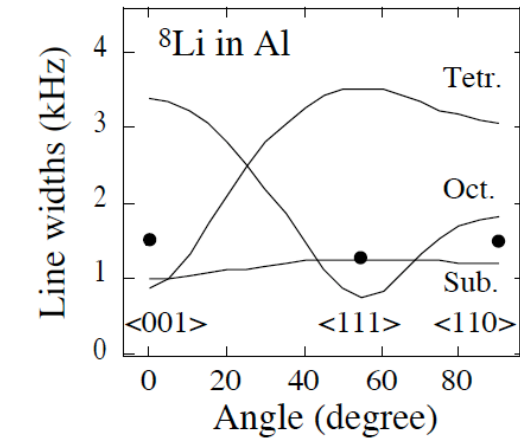
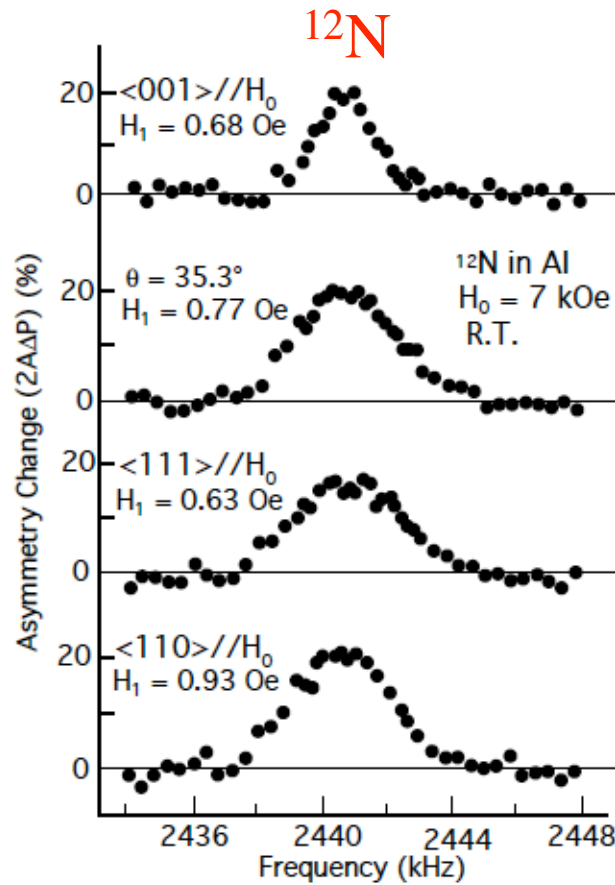
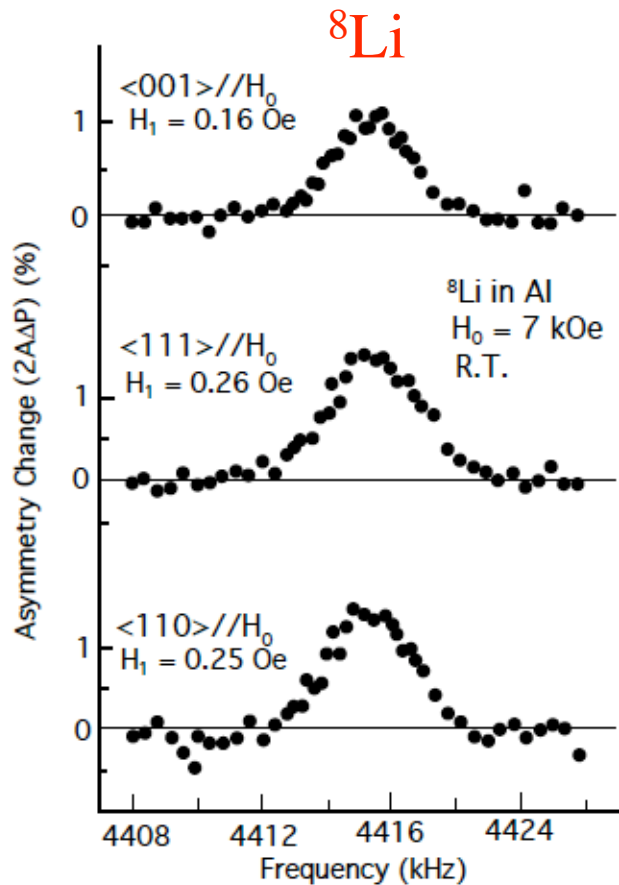


NMR線幅に影響を与える



不純物サイト決定

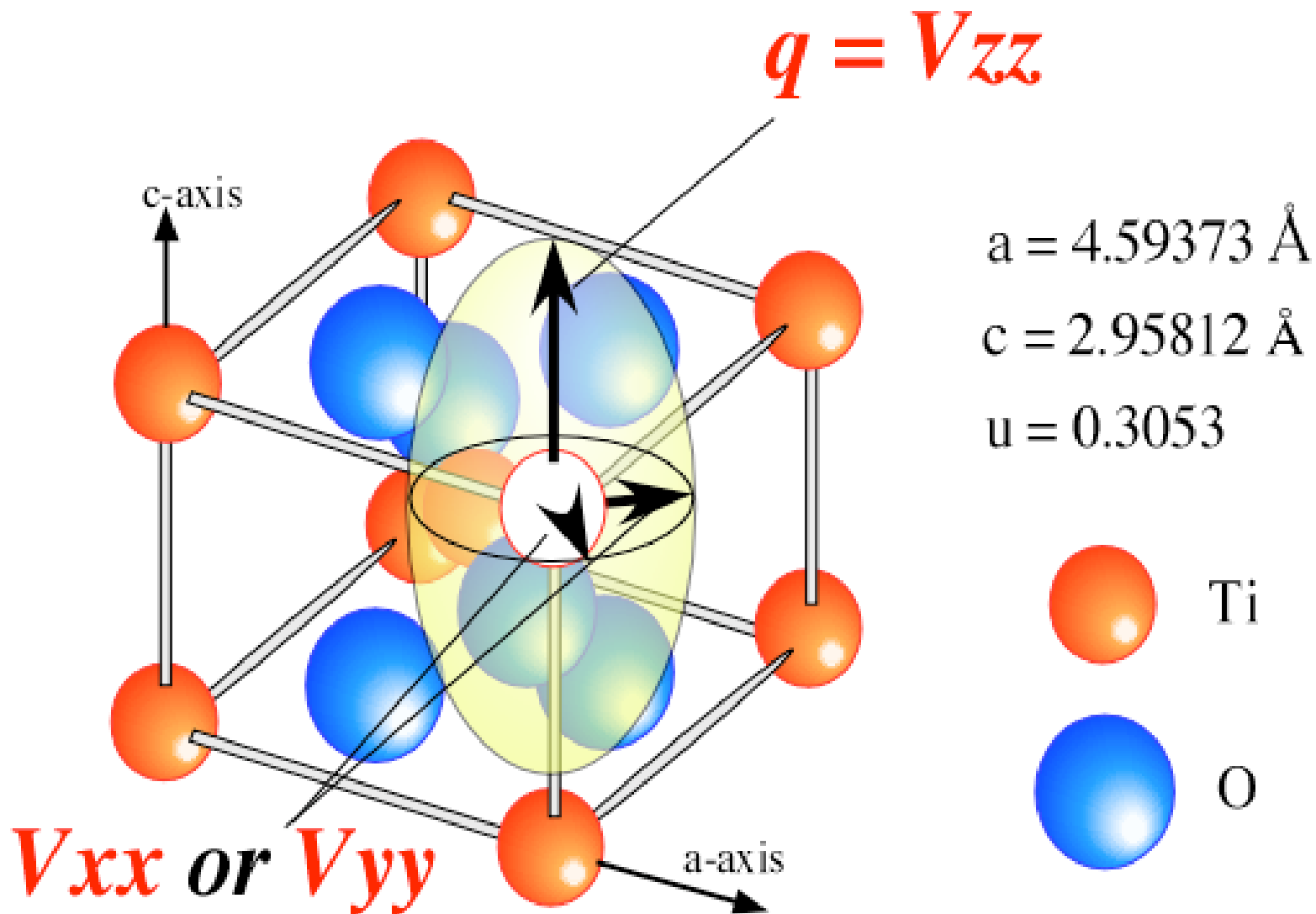
Al 単結晶中不純物のNMRスペクトル



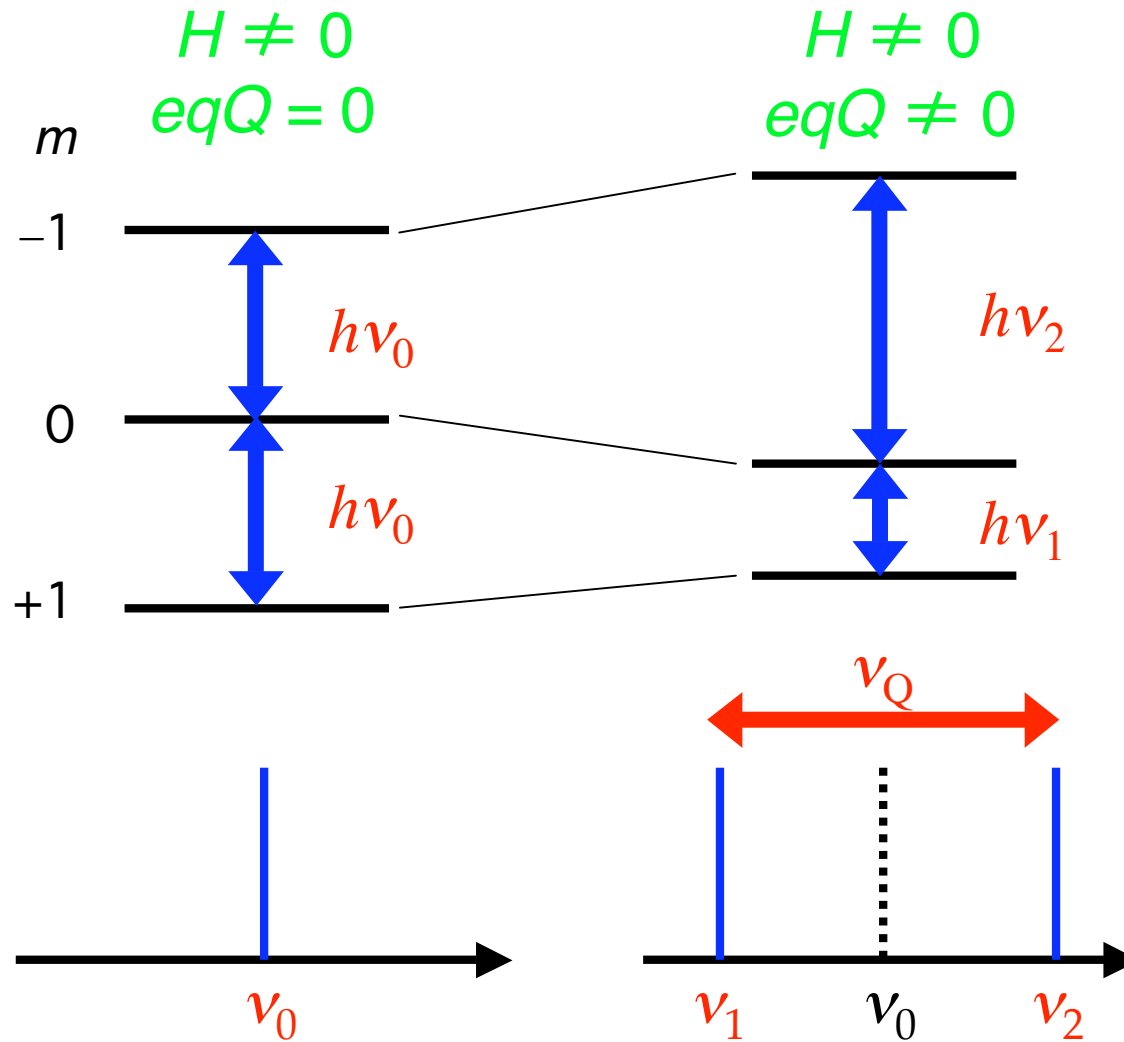
Impurities	in Cu	Ref.	in Al	Ref.
^8Li	Sub.	[3]	Sub.	present
^{12}B	Oct. + Sub.	[1][2]	Oct.	[4]
^{12}N	Oct.	[1]	Tetr.	present

Sub.: substitutional site, Oct.: octahedral interstitial site,
Tetr.: tetrahedral interstitial site

TiO₂ (ルチル) 中不純物の電場勾配

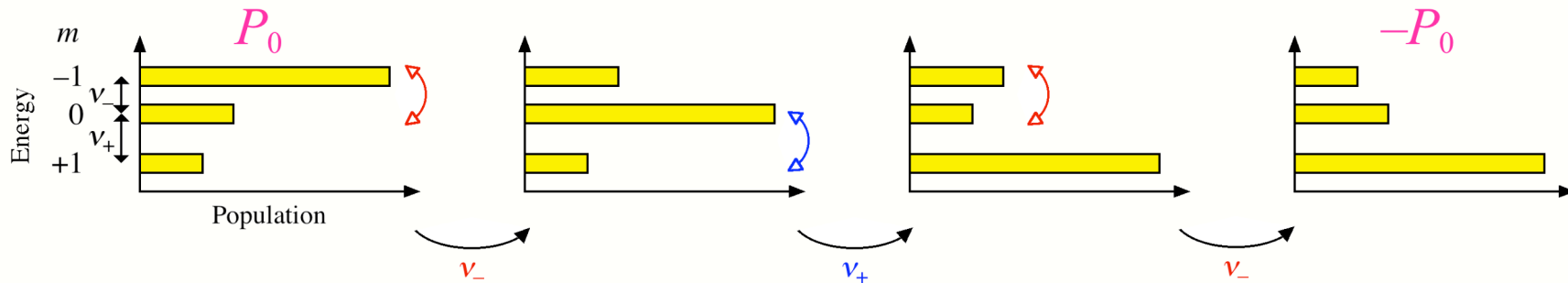


四重極相互作用による分裂



β -nuclear quadrupole resonance (β -NQR) method

using adiabatic fast passage (AFP) to invert polarization

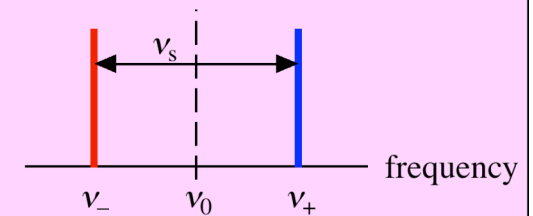


Symmetric EFG, high magnetic field limit for nuclear spin $I = 1$

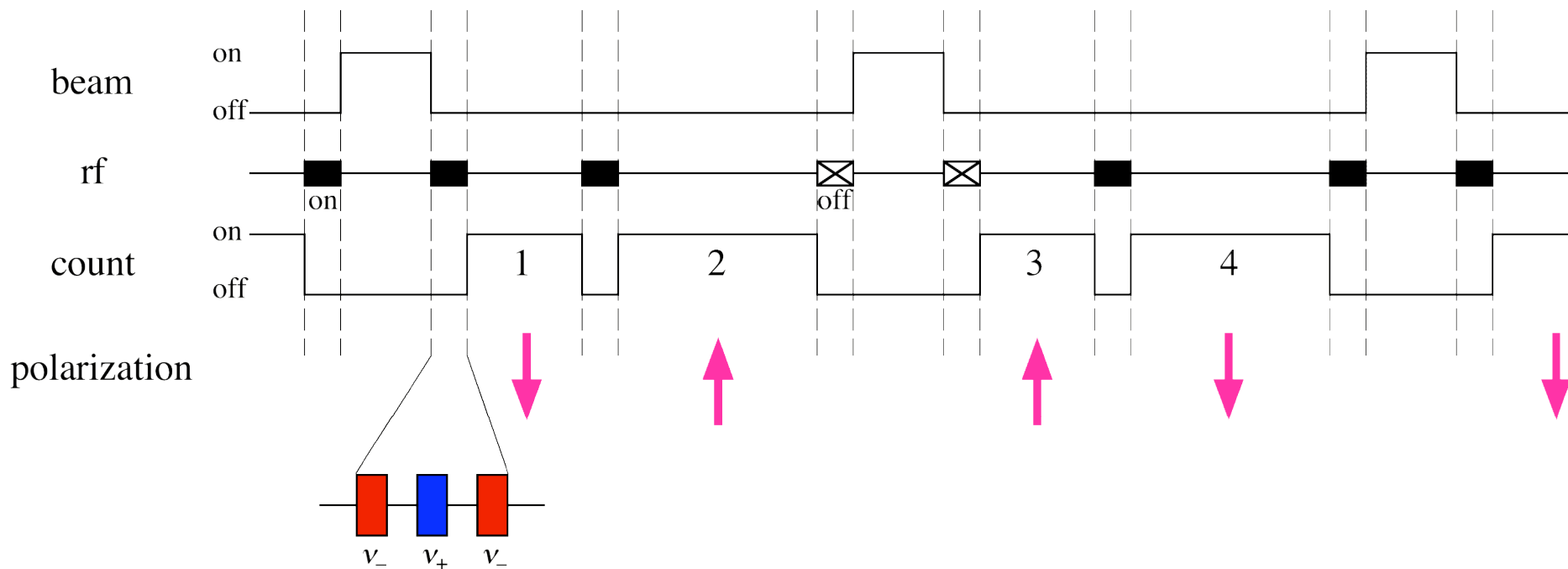
Resonance frequency; $\nu_{\pm} = \nu_0 \pm (\nu_Q/2)(3\cos^2\theta - 1)$

Separation frequency; $\nu_s = \nu_+ - \nu_- = \nu_Q(3\cos^2\theta - 1)$

$$\nu_0 = \mu H / (Ih), \quad \nu_Q = [3 / \{4I(2I-1)\}] (eqQ/h)$$



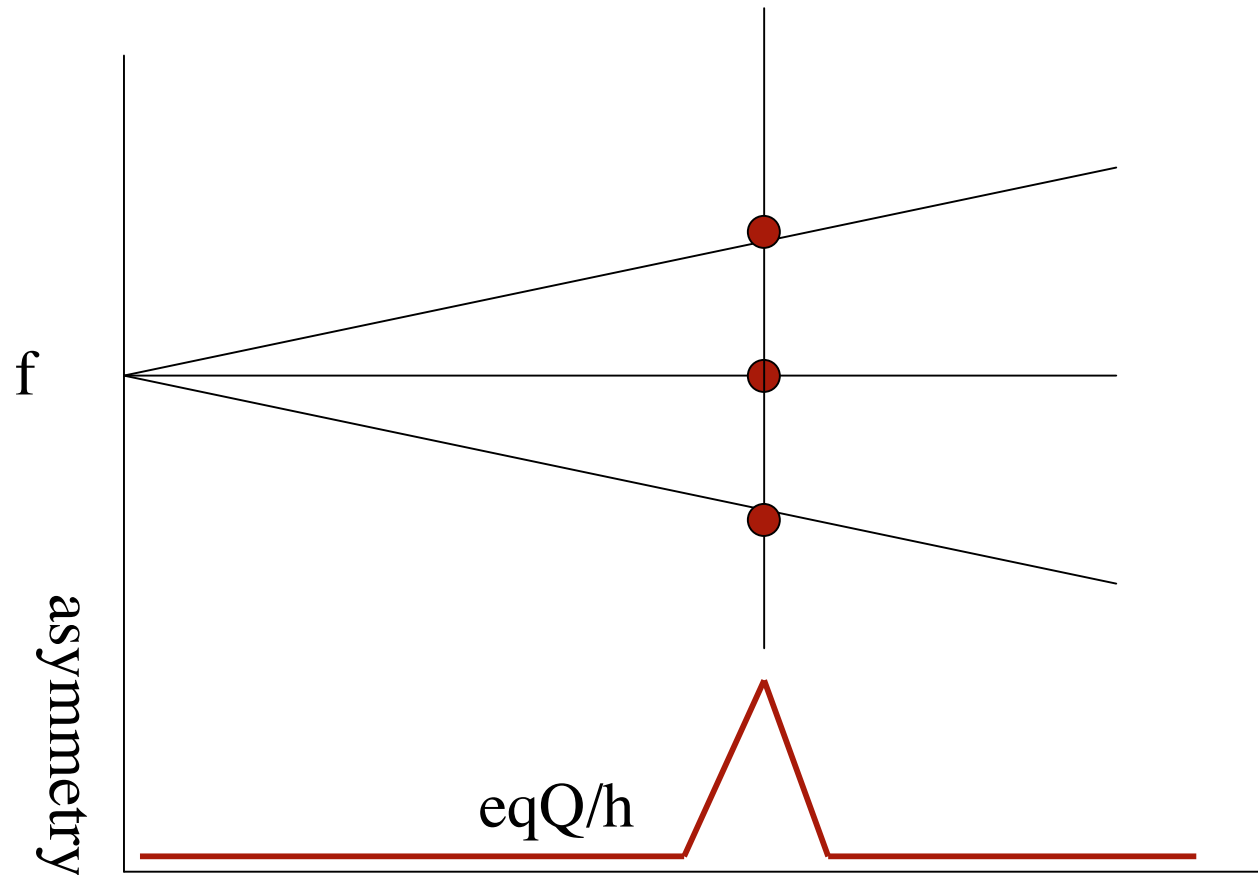
Time sequence for β -NQR measurement



β -ray asymmetry change; $AP = \frac{1 - \{(R_1 R_4)/(R_2 R_3)\}^{1/4}}{1 + \{(R_1 R_4)/(R_2 R_3)\}^{1/4}} \quad (R \equiv N_{\text{up}}/N_{\text{down}})$

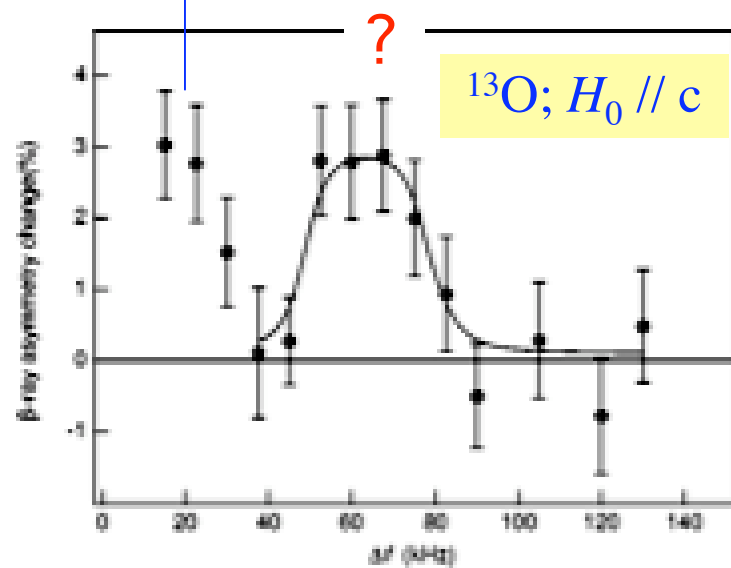
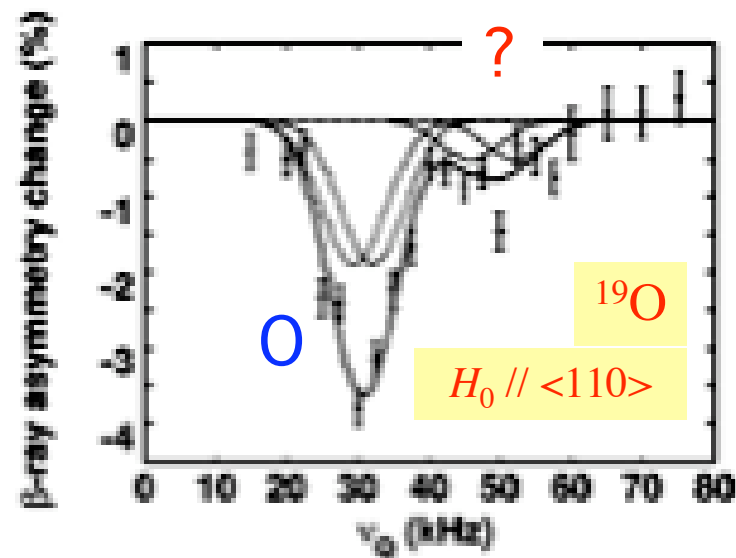
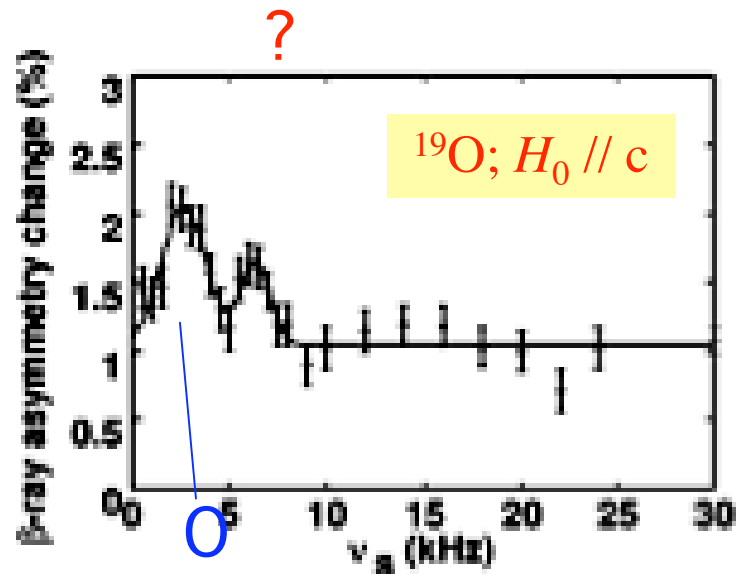
Multi-rf β -NMR/NQR

$I = 3/2$ case



ZnO or TiO_2

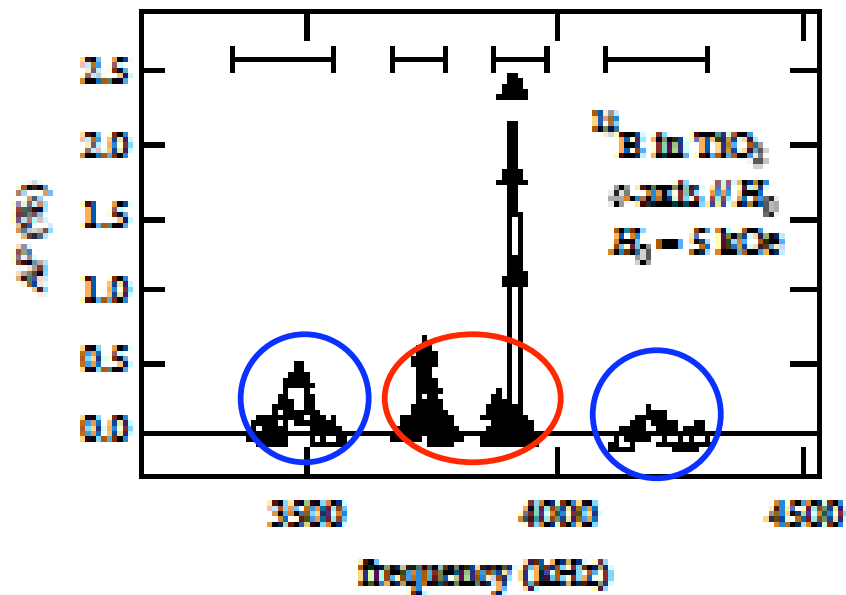
TiO₂ 中 ¹³O, ¹⁹O の電場勾配



O ; 酸素置換位置

? ; 格子間隙位置 ?

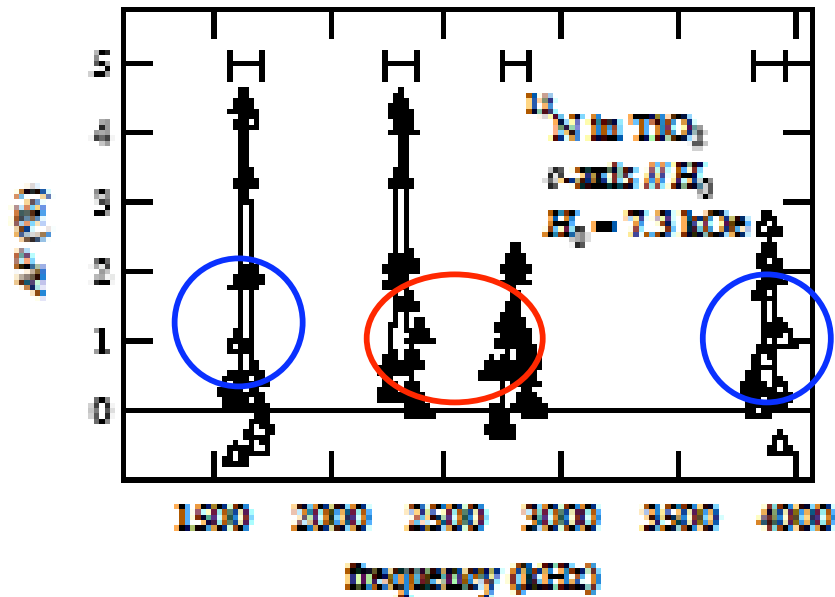
TiO₂ 単結晶中 ¹²B, ¹²N の NMR



¹²B ($I = 1$, $T_{1/2} = 20$ ms)

Ti 置換位置 90%

格子間隙位置 10%

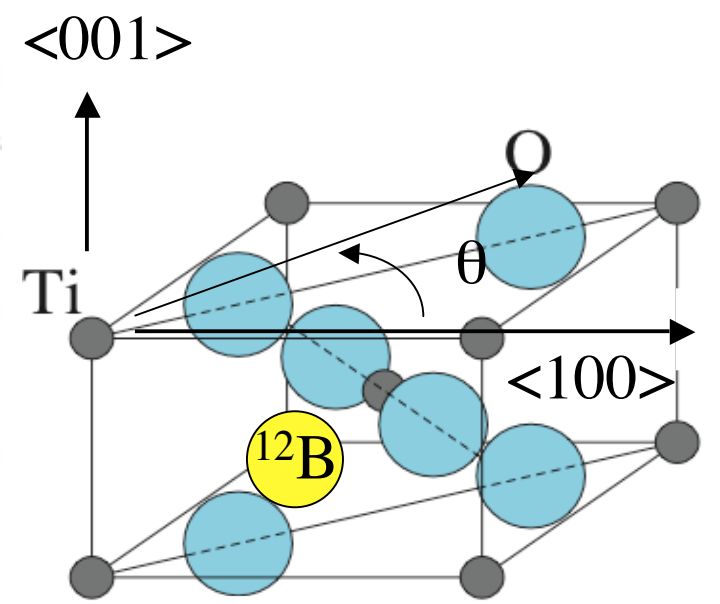
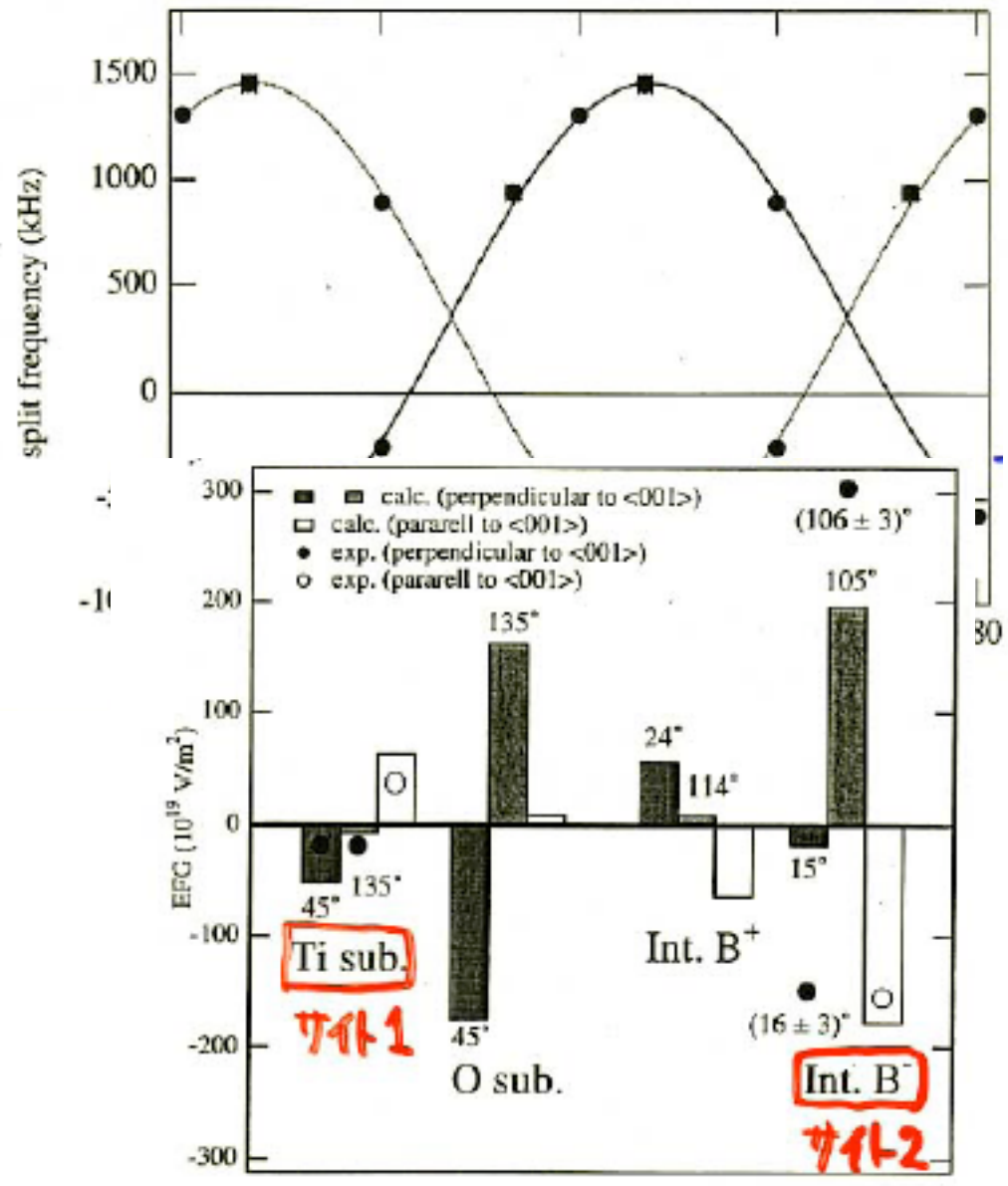


¹²N ($I = 1$, $T_{1/2} = 11$ ms)

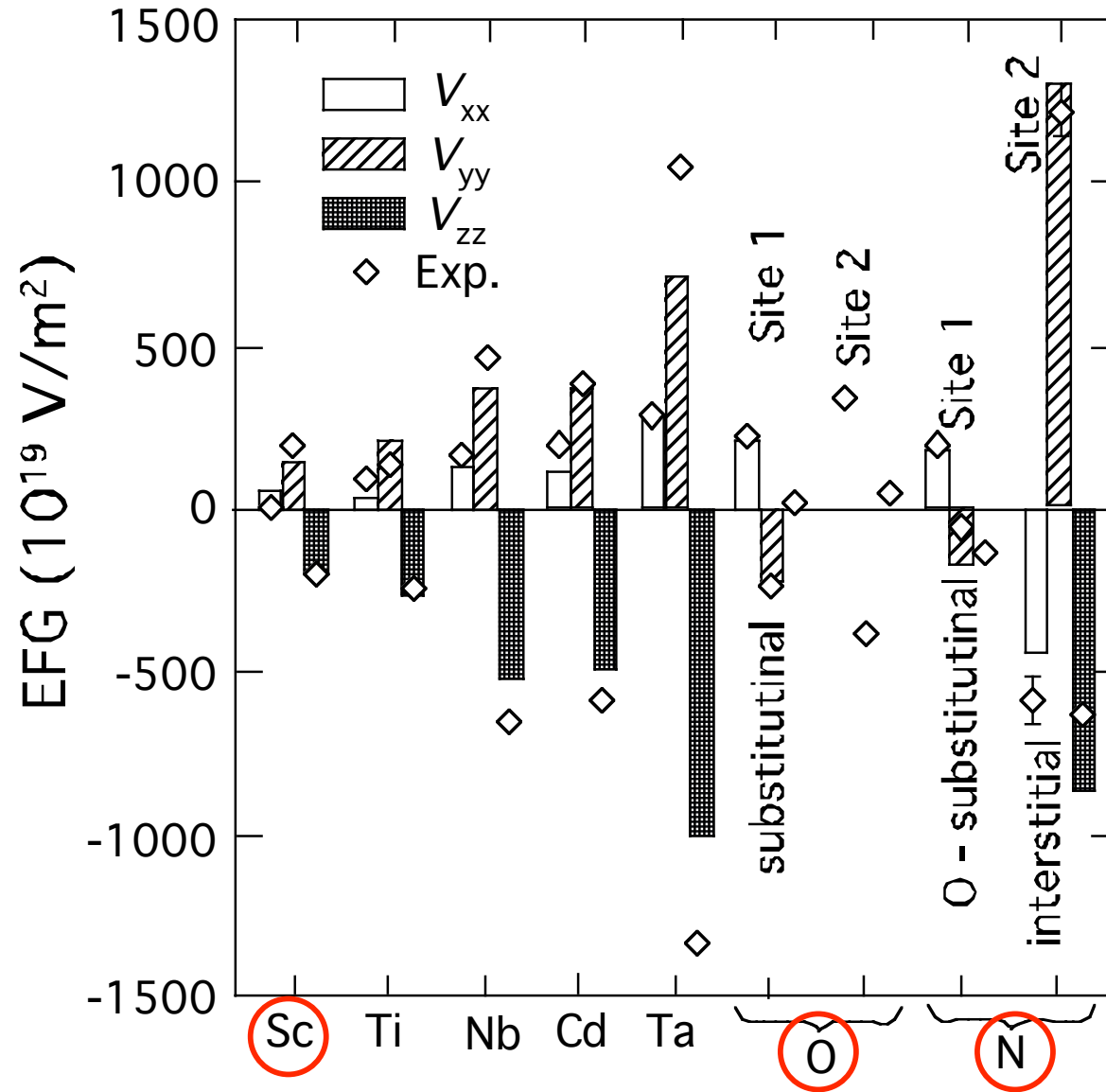
O 置換位置 50%

格子間隙位置 50%

^{12}B in TiO_2



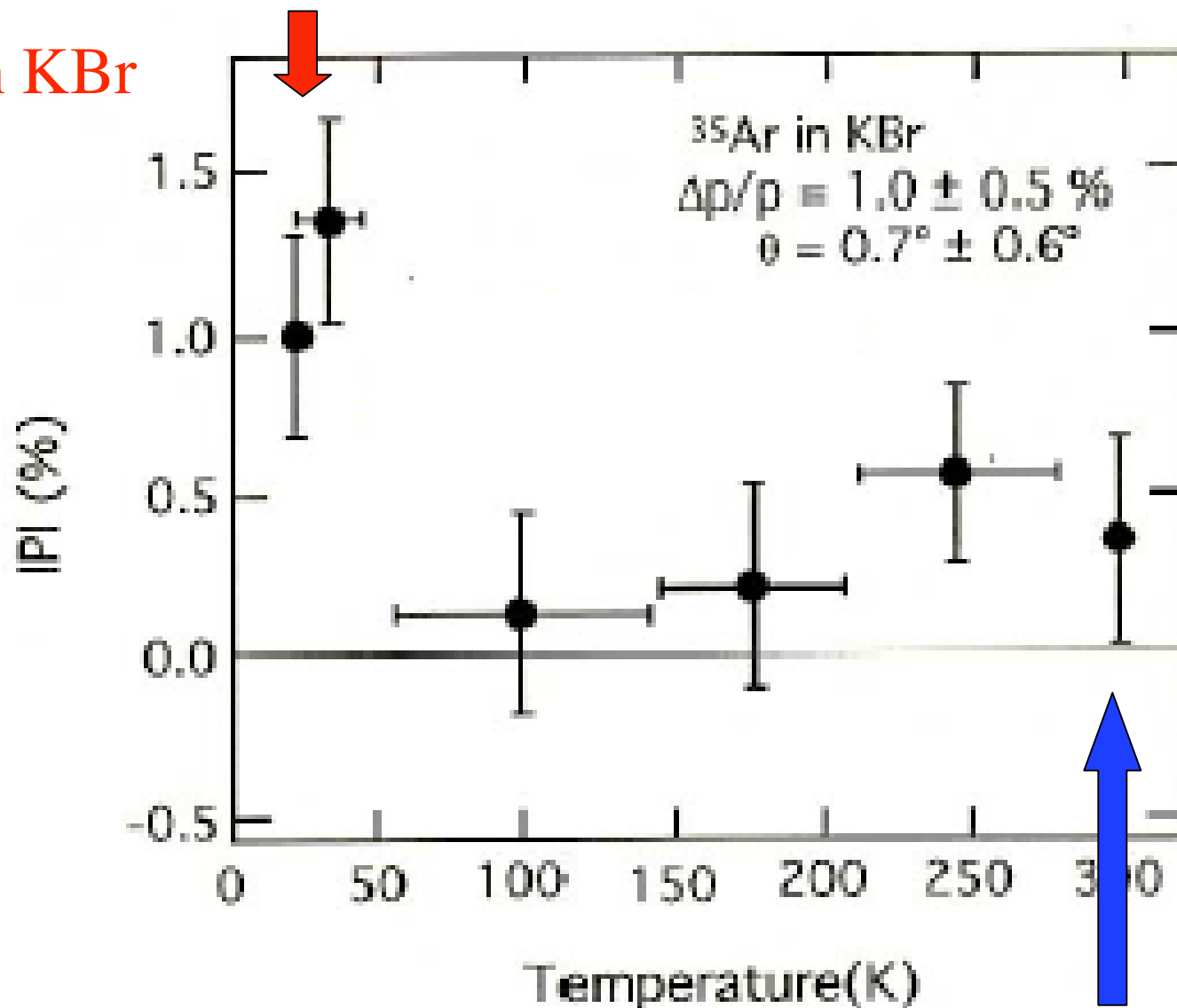
EFG prediction for TiO₂



動的挙動

固体中希ガス元素の挙動

³⁵Ar in KBr



TiO₂ 中 N の動的挙動

TiO₂ バンドギャップ

N ドープ (O 置換)

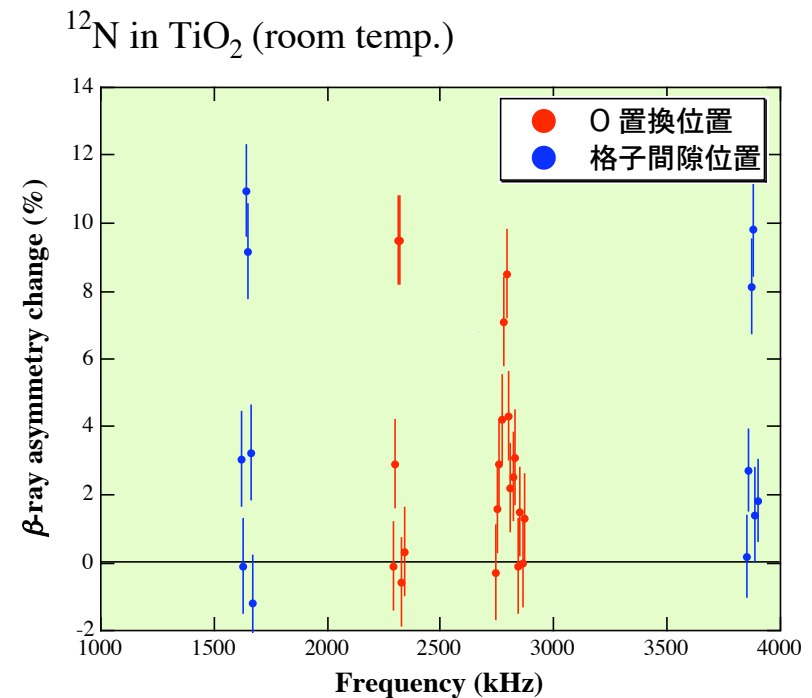
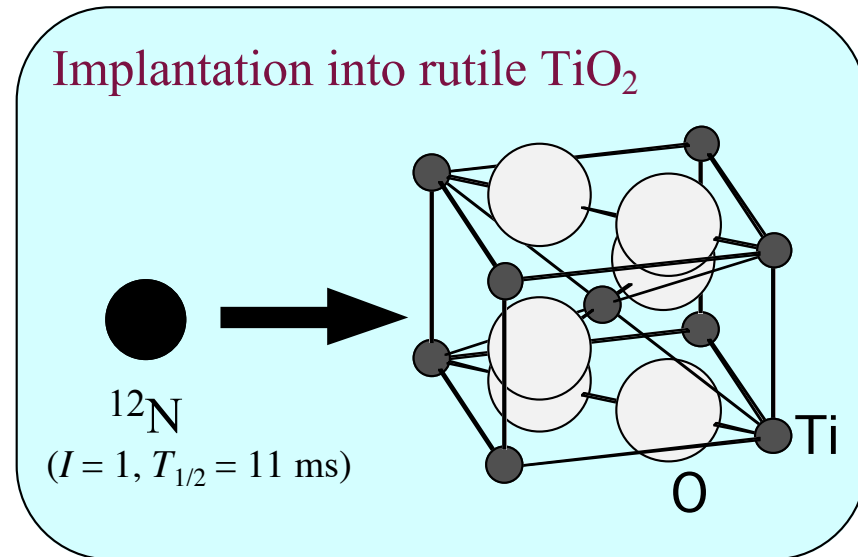
~3 eV (UV)

可視領域

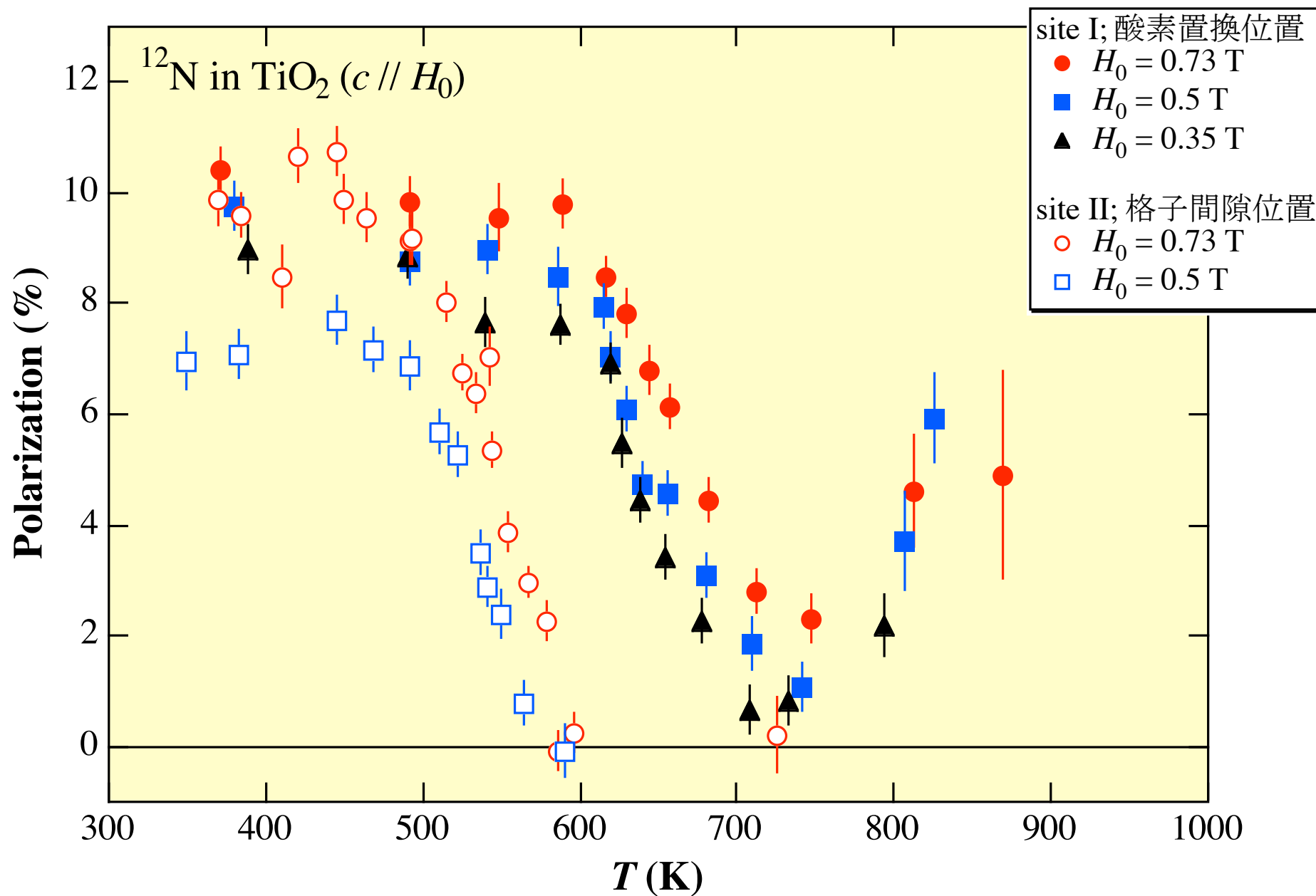
光触媒作用の可視光応答化

R. Asahi et al., Science **293** (2001) 269

N in TiO₂ is
Stable ? or Diffusive ?

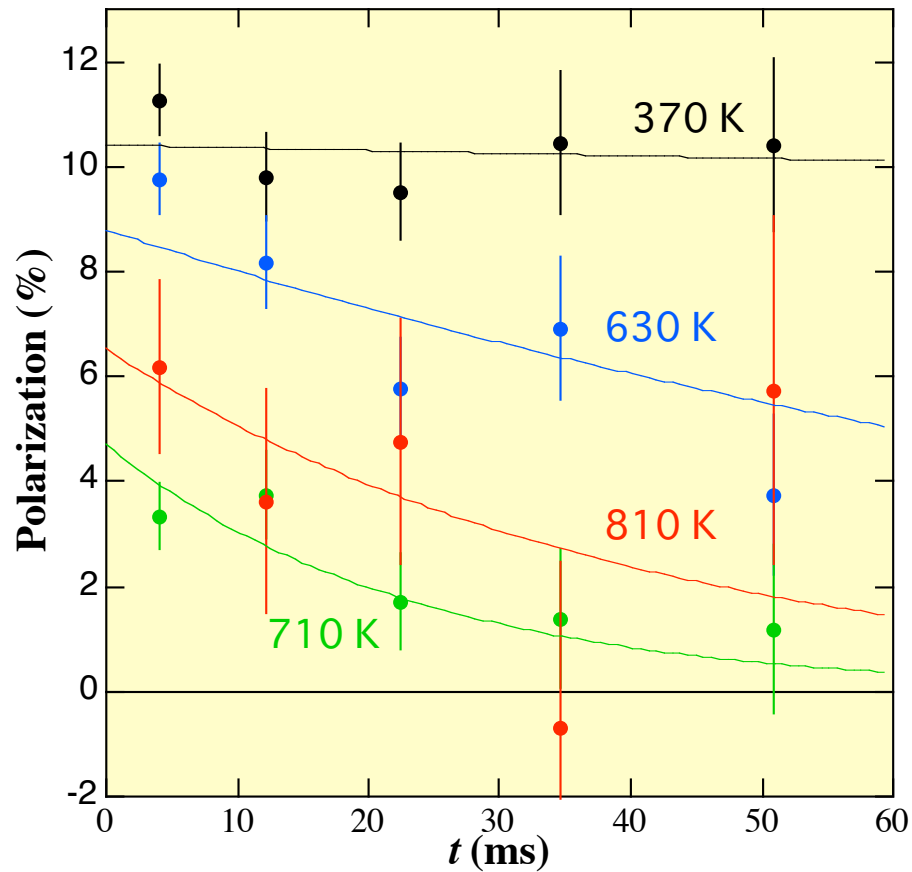


TiO₂中¹²Nの偏極の温度依存性

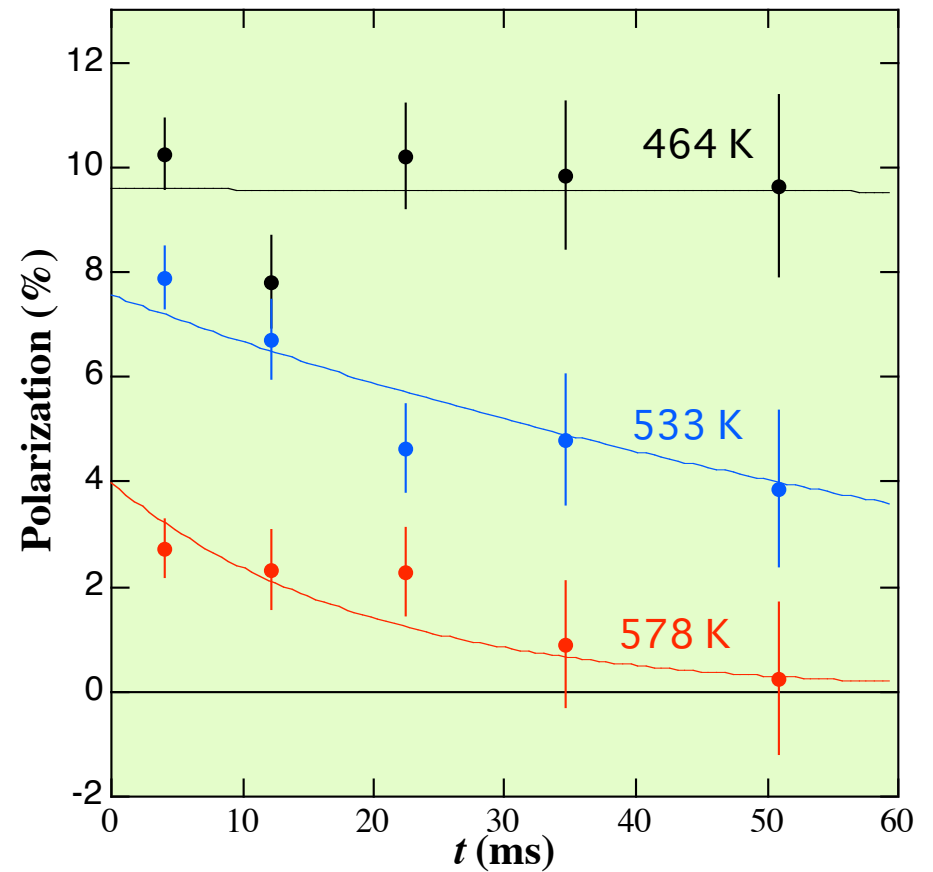


TiO₂中¹²Nの偏極の時間変化

酸素置換位置



格子間隙位置



原子ジャンプによるスピン格子緩和

$$\frac{1}{T_1} \propto \langle \omega_Q^2 \rangle \{k_1(\omega_0) + 4k_2(2\omega_0)\}$$

$$k_n(\omega_0) = \frac{\tau_c}{2\{1 + (n\omega_0\tau_c)^2\}}$$

$$1/\tau_c = \nu_0 \exp(-E_a/kT)$$

$\langle \omega_Q^2 \rangle$: mean fluctuation of the quadrupole field

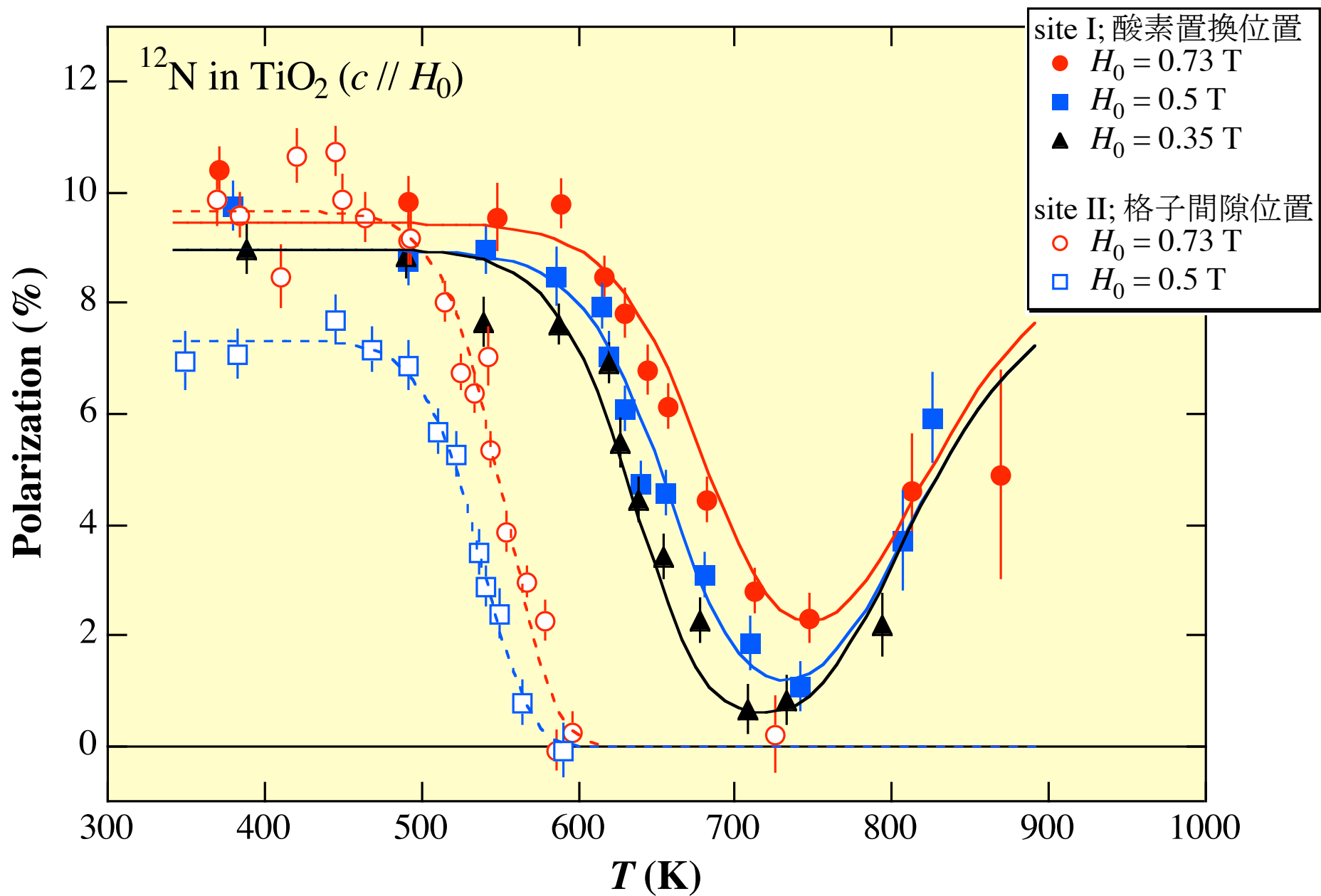
ω_0 : Larmor frequency

τ_c : correlation time

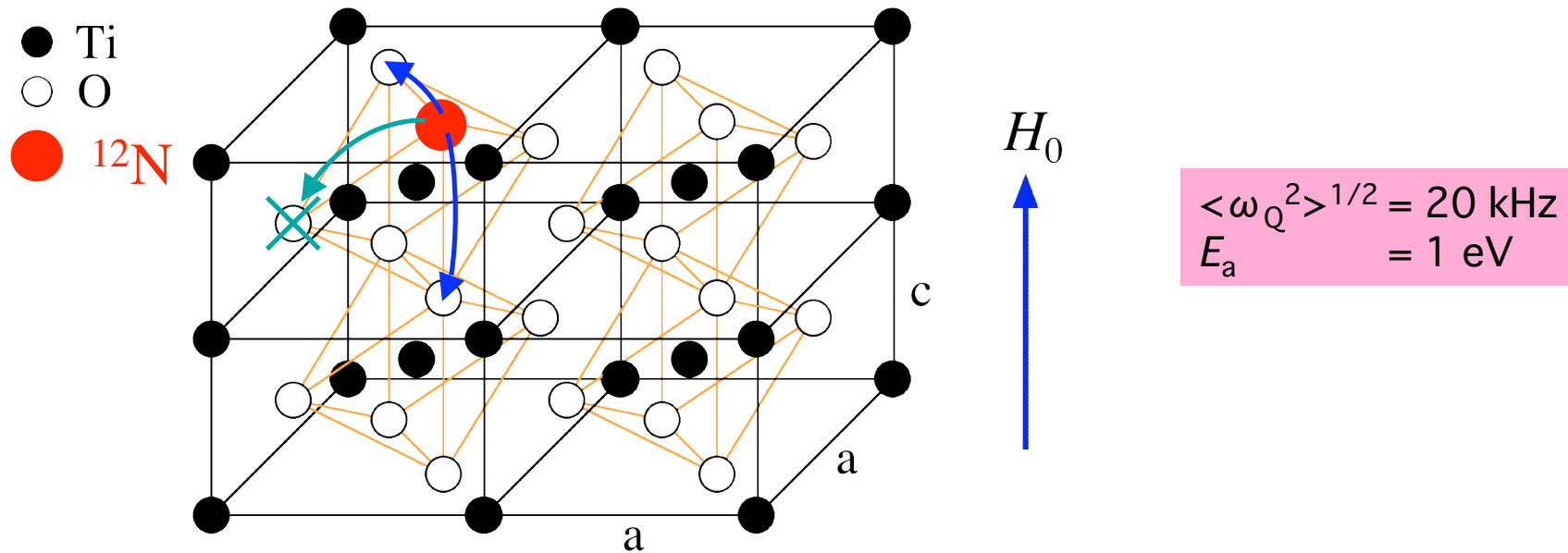
ν_0 : jump frequency at infinite temperature

E_a : activation energy

Fitting 結果

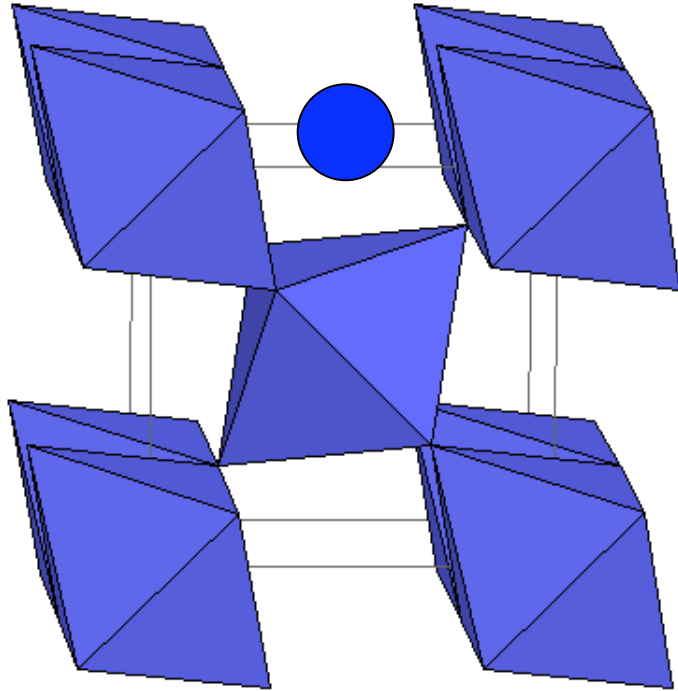


Behavior of substituted N atoms



- ✗ 1. Jumps between substitutional sites ?
related with O vacancy diffusion; $E_a > 2 \text{ eV}$
- 2. Motion of defects around substituted ^{12}N atoms ?
It is not clear that what kind of defect is responsible for $1/T_1$.

Behavior of interstitial N atoms



charge state; (predicted by Ogura et al.)

N^{3-} (O sub.)

N^- (Int.) ← smaller

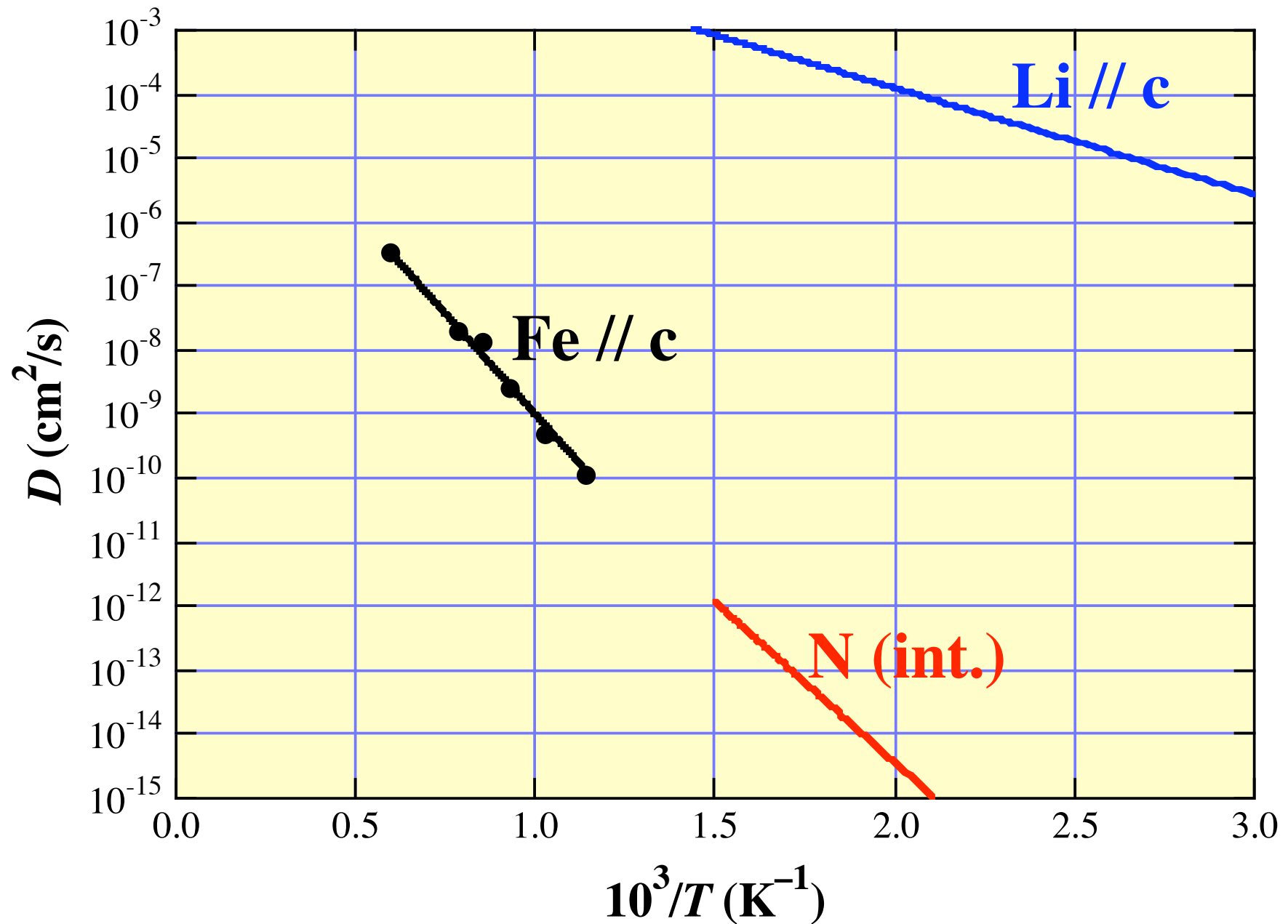
Interstitial ^{12}N atom might be
diffusive along the *c* axis.



$\langle \omega_Q^2 \rangle^{1/2} \sim$ static quadrupole field
 ~ 2.8 MHz

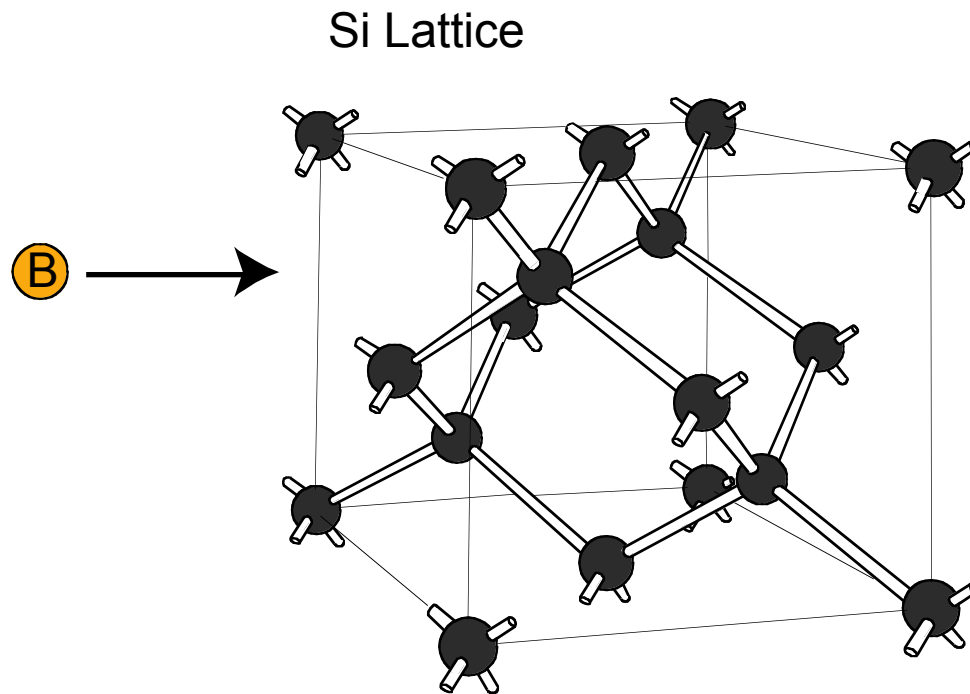
E_a	$= (1.0 \pm 0.2) \text{ eV}$
ν_0	$= (1 \times 10^9 - 1 \times 10^{13}) \text{ s}^{-1}$

TiO₂ (ルチル) 中不純物の拡散係数



Si 中 B の動的挙動

T. Izumikawa et al.

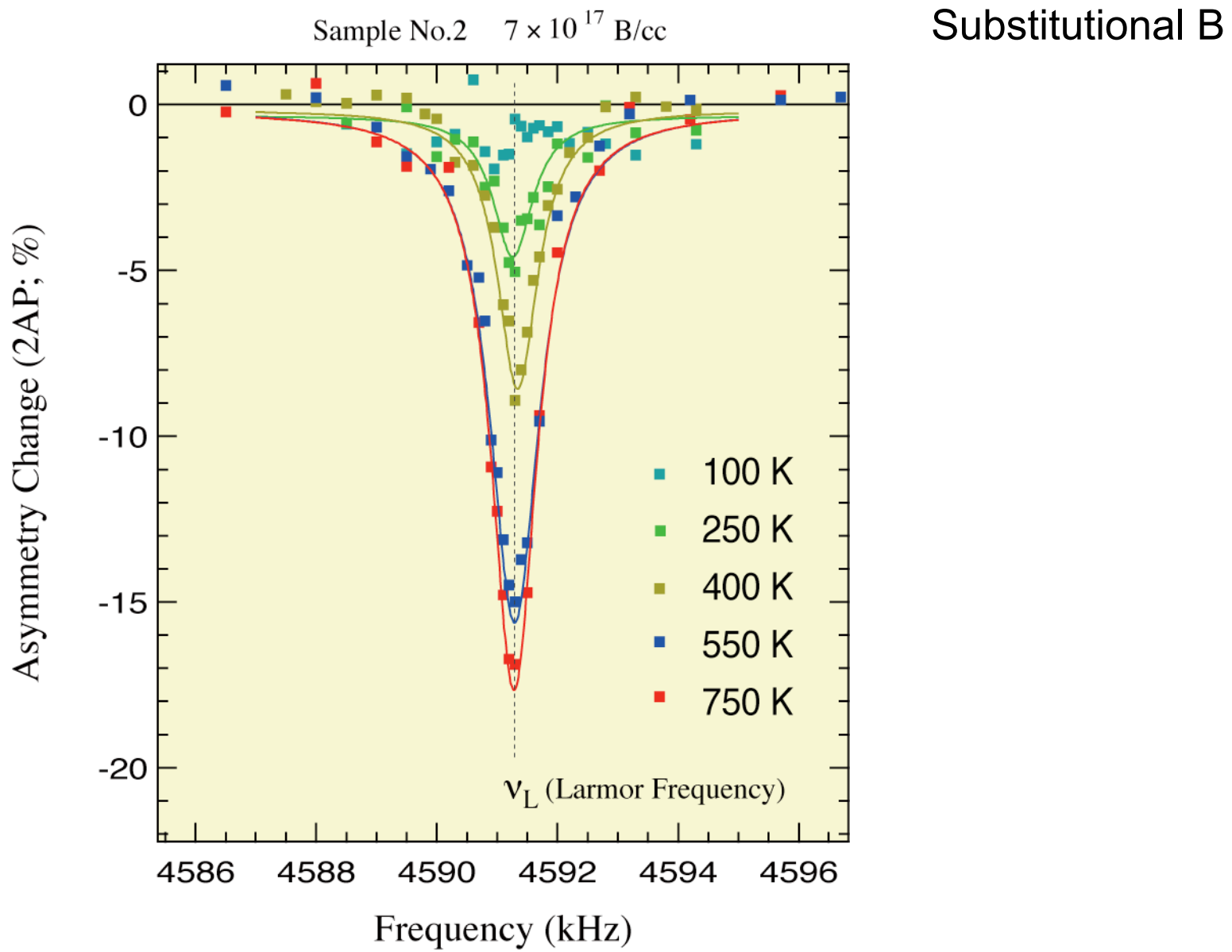


- ・ p 型シリコン生成
- ・ B イオンインプラ
ンテーション

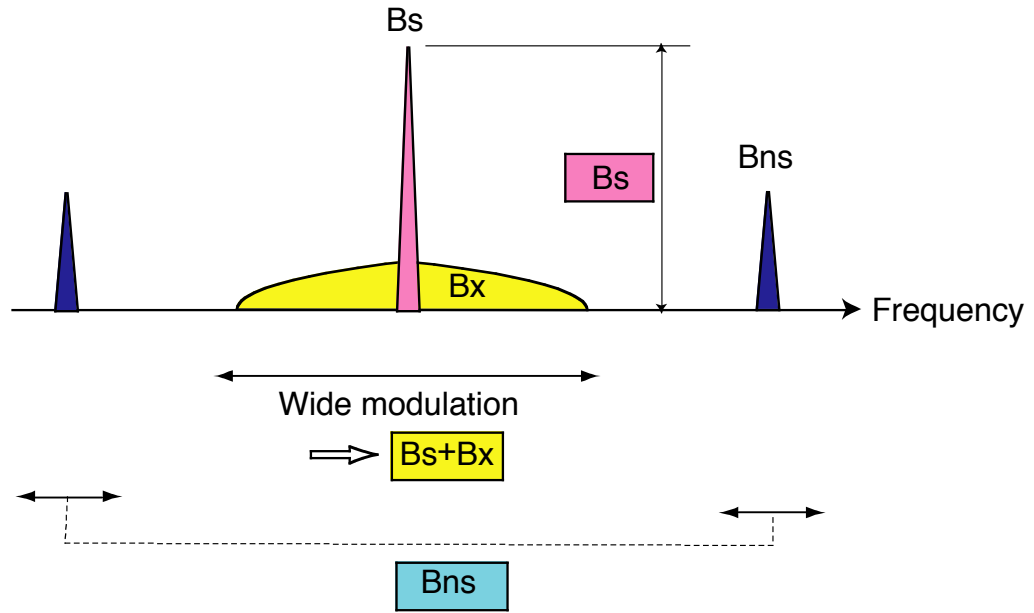
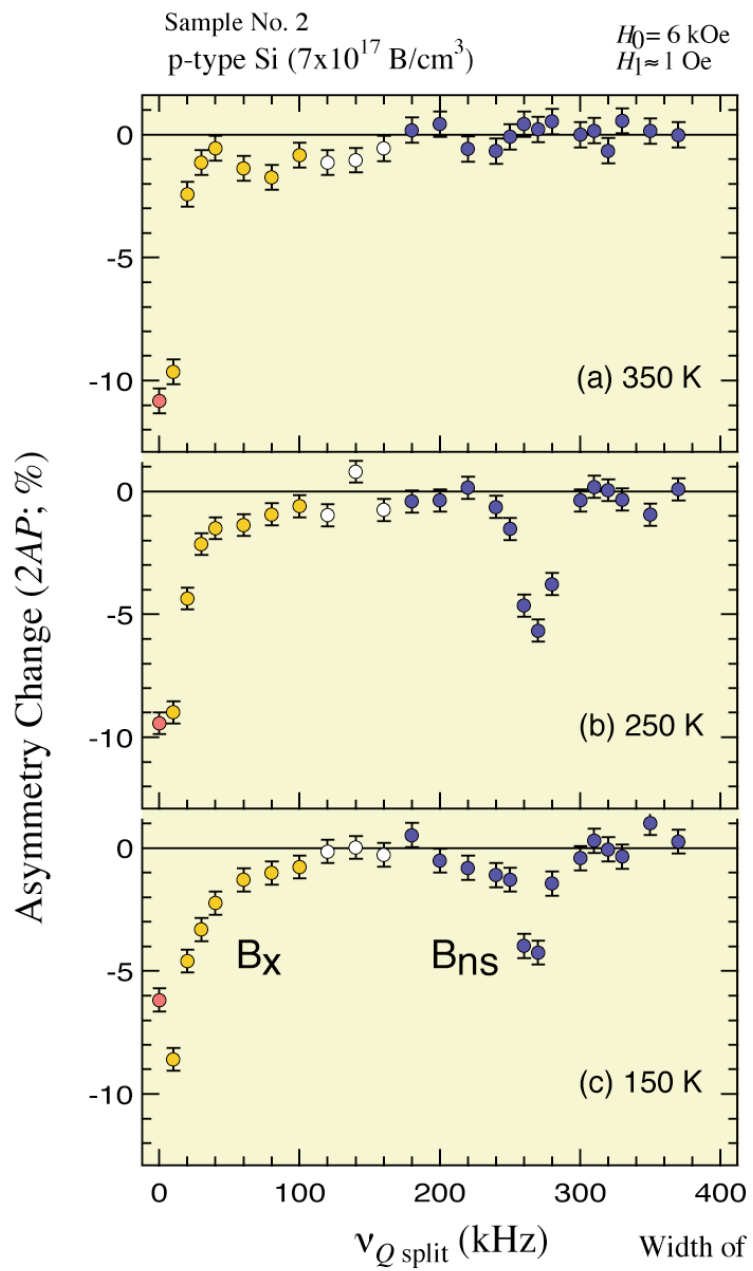
Lattice constant $a = 5.43 \text{ \AA}$

$$\left(\frac{\sqrt{3}}{4} a = 2.35 \text{ \AA} \right)$$

NMR Spectrum at Larmor Frequency

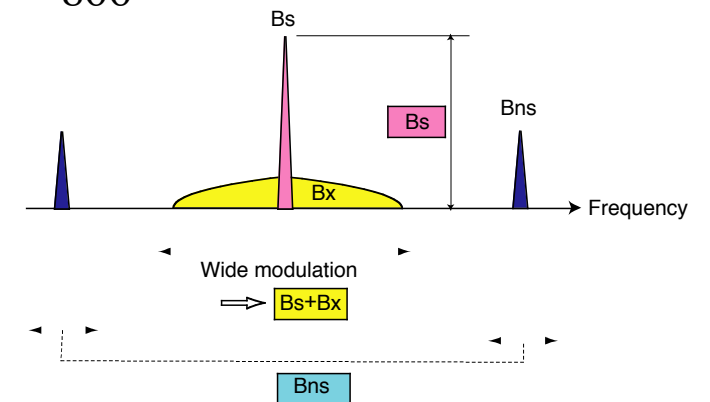
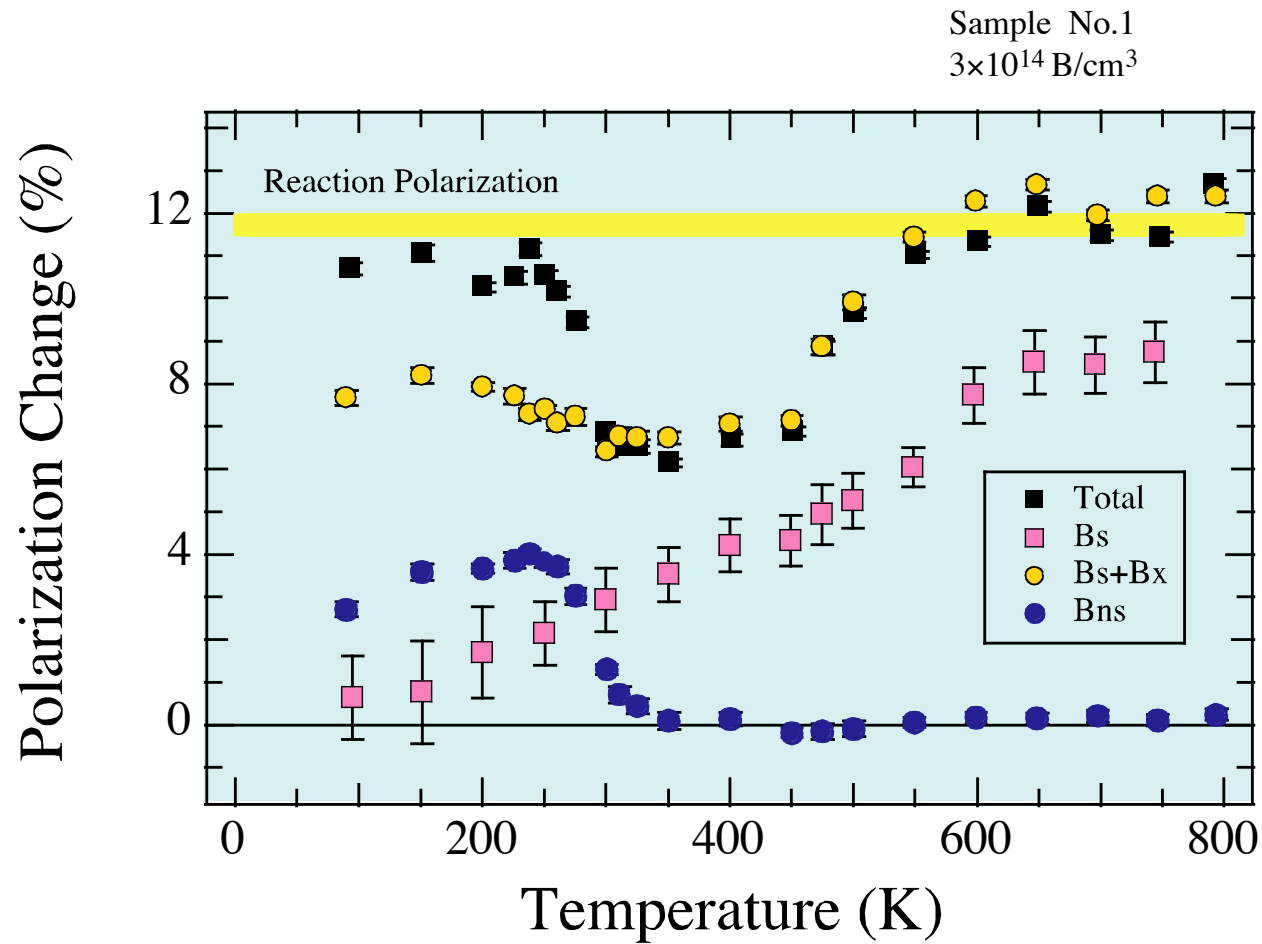


β-NQR Spectrum



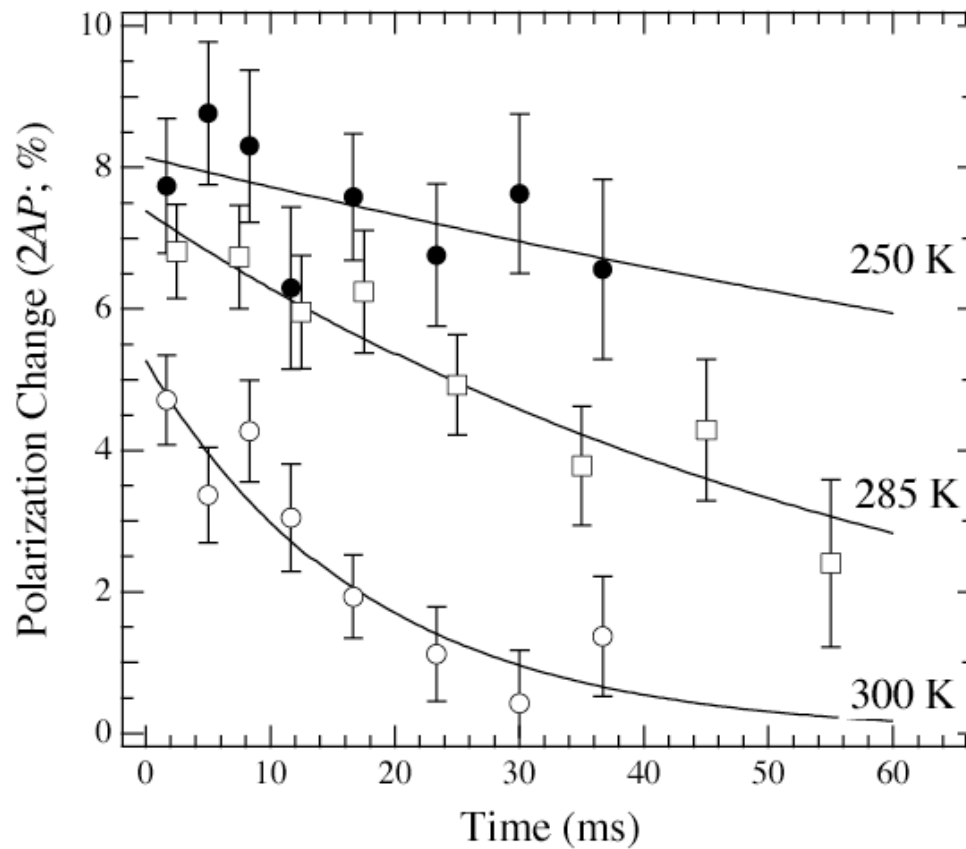
- 3種類の共鳴線
1. 鋭い共鳴 → 置換位置(Bs)
 2. 四重極分裂した共鳴 → $\langle 111 \rangle$ 対称位置(Bns)
 $eqQ/h = 364 \pm 7$ kHz
 3. ν_L 近傍に広がった共鳴 → B x

Temperature Dependence of Polarization Change



Spin-Lattice Relaxation of Bns

Relaxation of Polarization
p-type Si ($7 \times 10^{17} \text{ B/cm}^3$) sample No.2

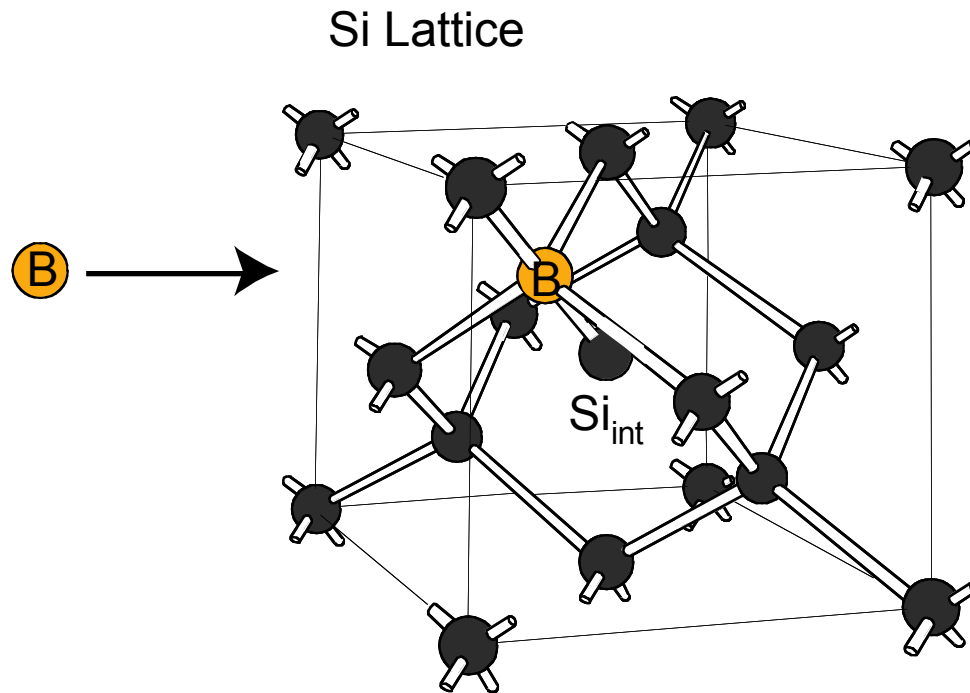


室温付近で偏極が観測されなくなっている原因は、速いスピ
ン格子緩和のためと
わかる。

速い Spin-Lattice relaxation の原因

1. 核の周囲の電場勾配の揺動
 2. 核の周囲の双極子場の揺動
 - × ^{29}Si ($m = -0.55\text{mN}$) の存在比が小さい
 3. 伝導電子との相互作用
 - × 伝導電子の密度が小さい
 4. Boron 原子の拡散に伴う、低対称性を持つサイトによるトラップ
 Δq の主軸の変化が説明できない
- 1 だけが、速い核偏極の緩和と q の主軸の変化を矛盾なく説明できる

B(Substitutional)-Si(interstitial) Model



- Bond Center
 - Interstitial
- ではなく
Bs-Si_i pair が安定

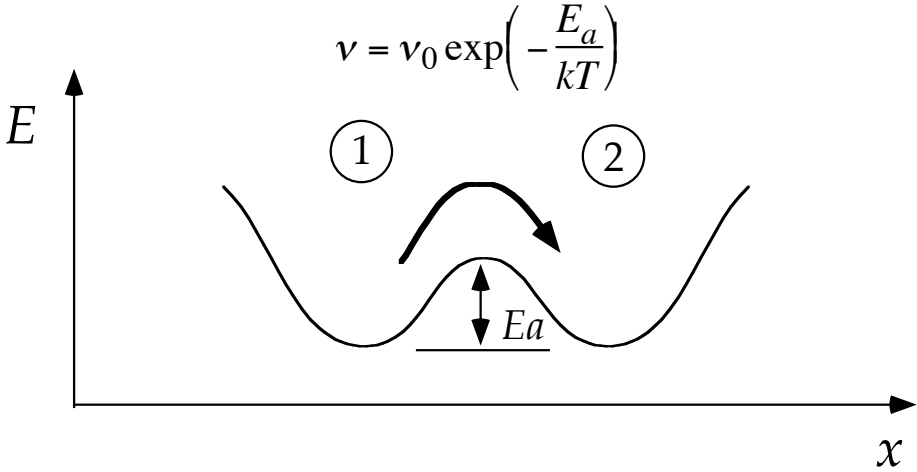
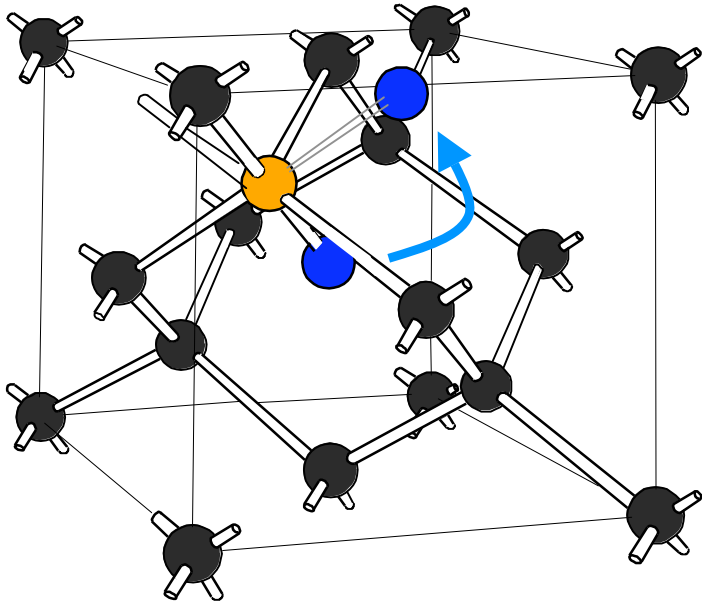
Tarnow, Europhys.Lett. **16**,449(91)

Lattice constant $a = 5.43 \text{ \AA}$

$$\left(\frac{\sqrt{3}}{4} a = 2.35 \text{ \AA} \right)$$

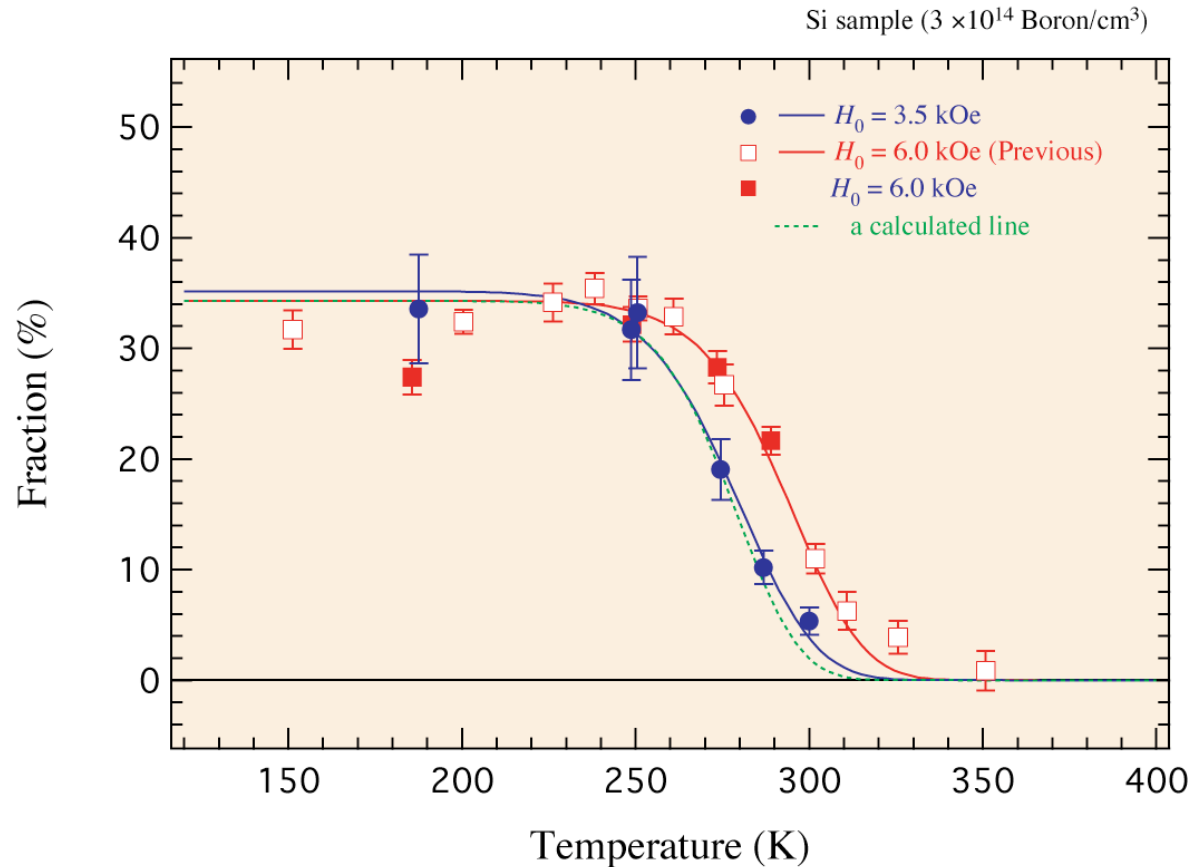
Atomic Jump of Bns

局所的原子ジャンプ



格子欠陥の等価な位置を熱活性的にジャンプする。

Spin-Lattice Relaxation of Bns



◆ 室温付近における、Bns (<111>対称の欠陥)原子の偏極の急激な減少は、揺動する電場によって引き起こされる。

◆ 欠陥原子は等価な位置間を熱的にジャンプしている。
その活性化エネルギーは
 0.45 ± 0.09 eV

Fitting results

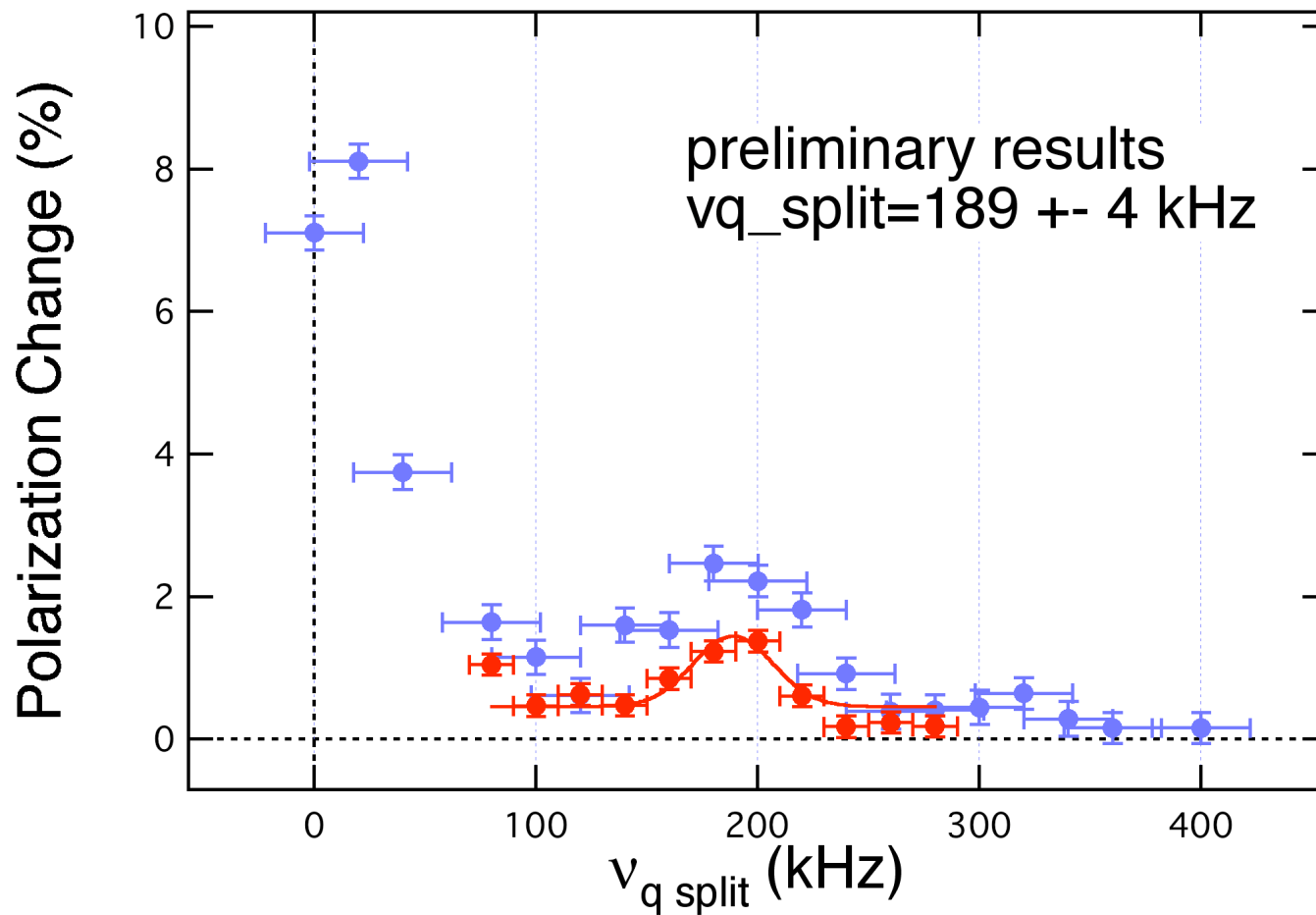
$$\nu \text{ (at 3.5kOe)} = 1.3 \times 10^8 \exp\left\{-\frac{(0.40 \pm 0.04) \text{ eV}}{kT}\right\} \text{ kHz}$$

$$\nu \text{ (at 6kOe)} = 1.5 \times 10^9 \exp\left\{-\frac{(0.46 \pm 0.07) \text{ eV}}{kT}\right\} \text{ kHz}$$

12B in Ge

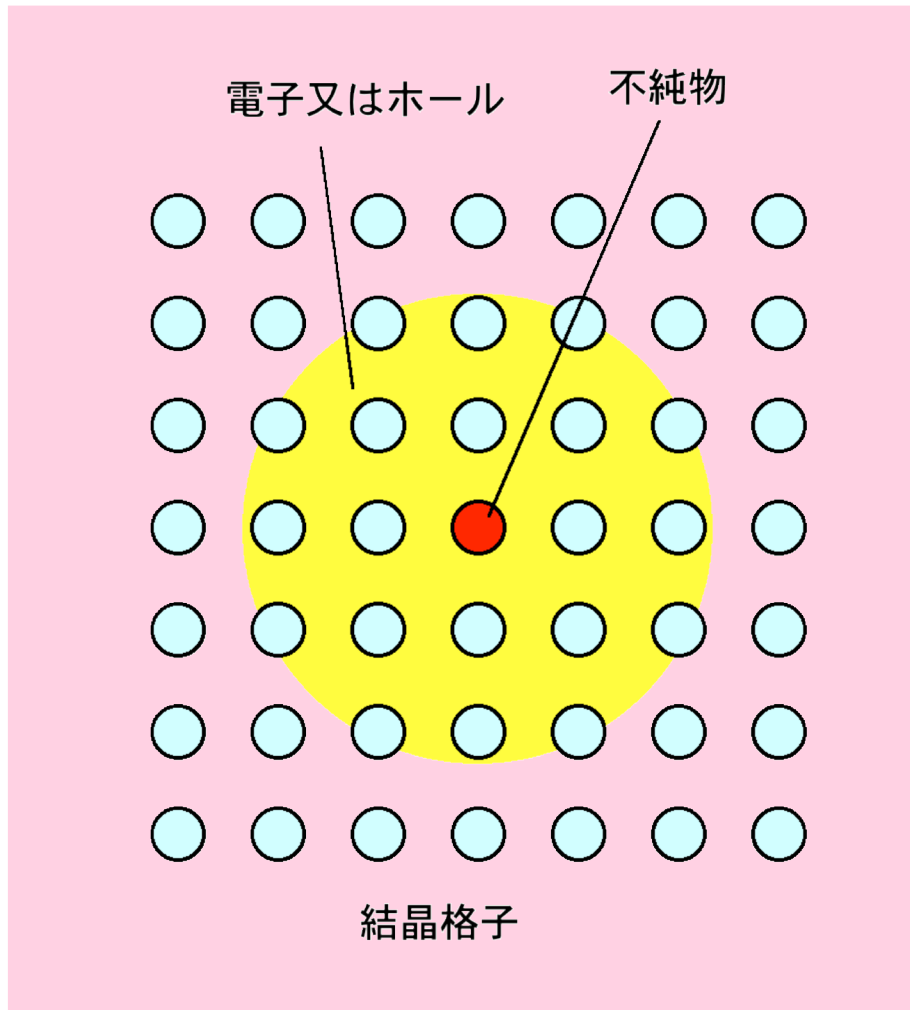
$\sim 10^{14}$ In (cm^{-3})

(P-Type(In dope); 10~50 OhmCm), Temperature ~ 200 K



不純物準位

半導体中の浅い不純物準位



$$E = \frac{13.6}{\epsilon^2} \frac{m^*}{m} \text{ eV} \quad (\sim \text{meV})$$
$$a = 0.53 \frac{\epsilon}{m^*/m} \text{ \AA} \quad (10 \sim 100 \text{ \AA})$$

TiO₂ (ルチル)

$\epsilon_a \sim 115, \epsilon_c \sim 250 @ 4 \text{ K}$

$m_h^*/m < 1$

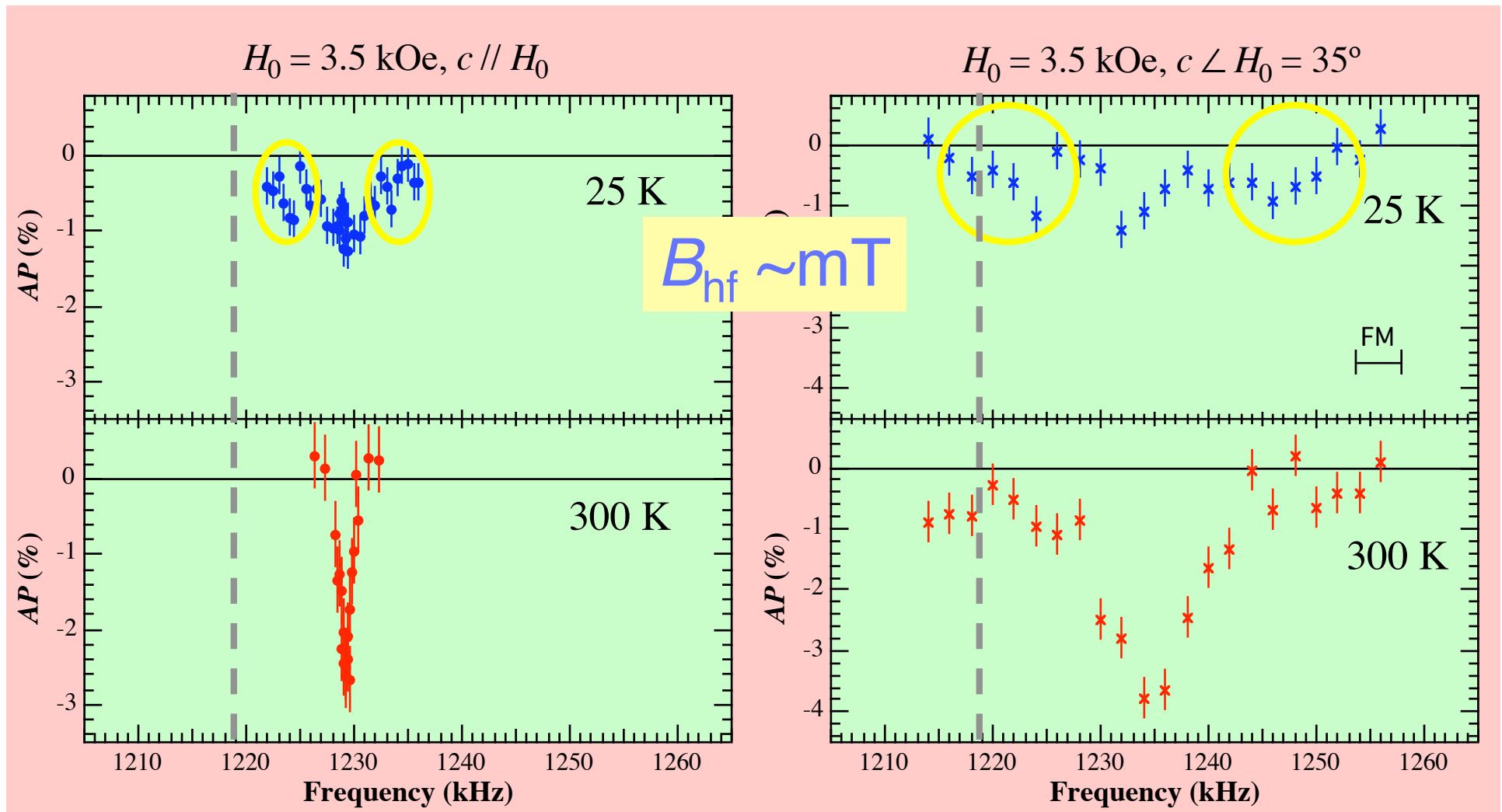
超微細相互作用 : $A_{\text{hf}} \propto |\Psi_e(0)|^2$

不純物核位置における超微細磁場 :

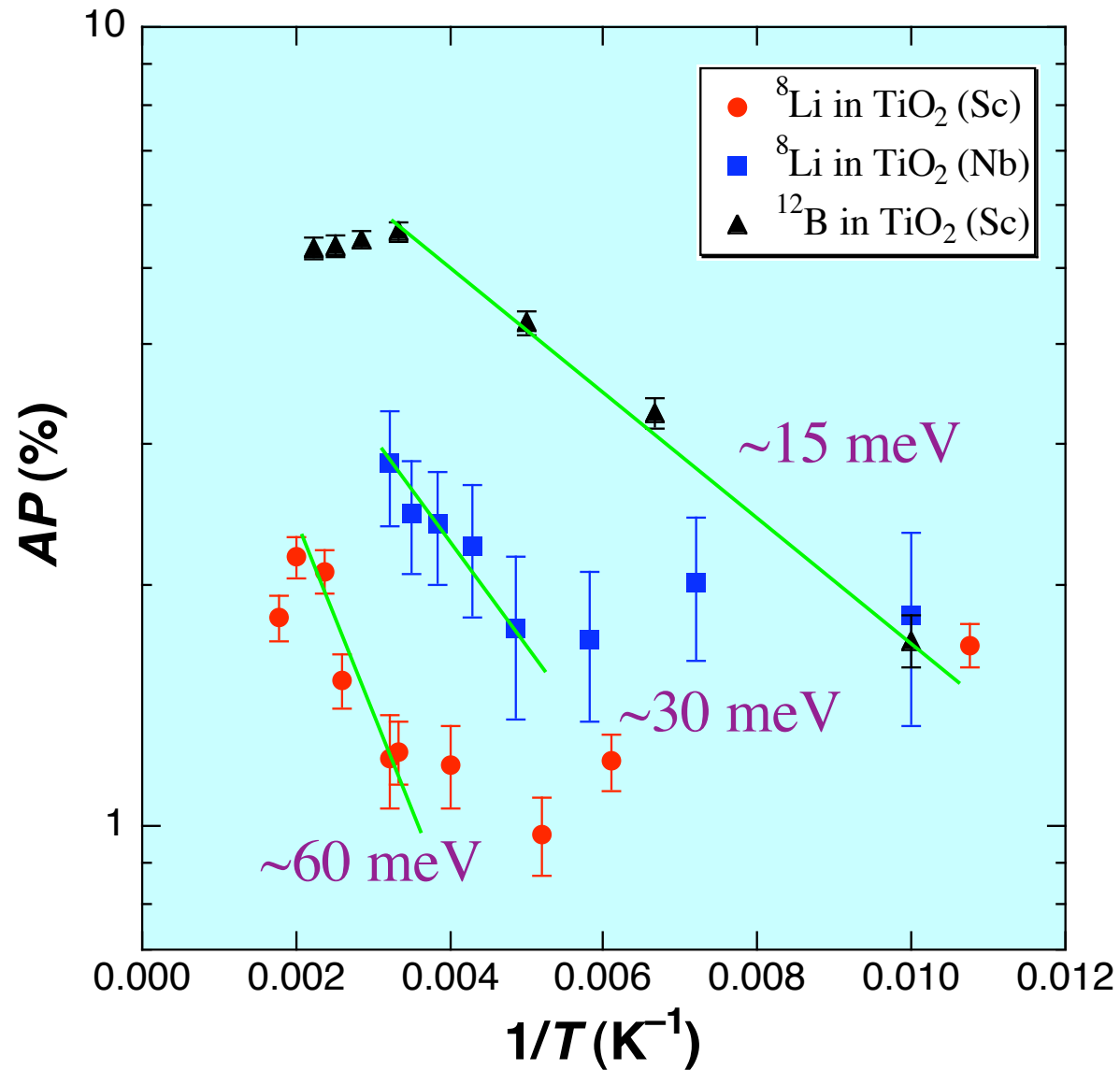
$B_{\text{hf}} \leq \sim \text{mT} ??$

β-NMR

^{12}N in TiO_2



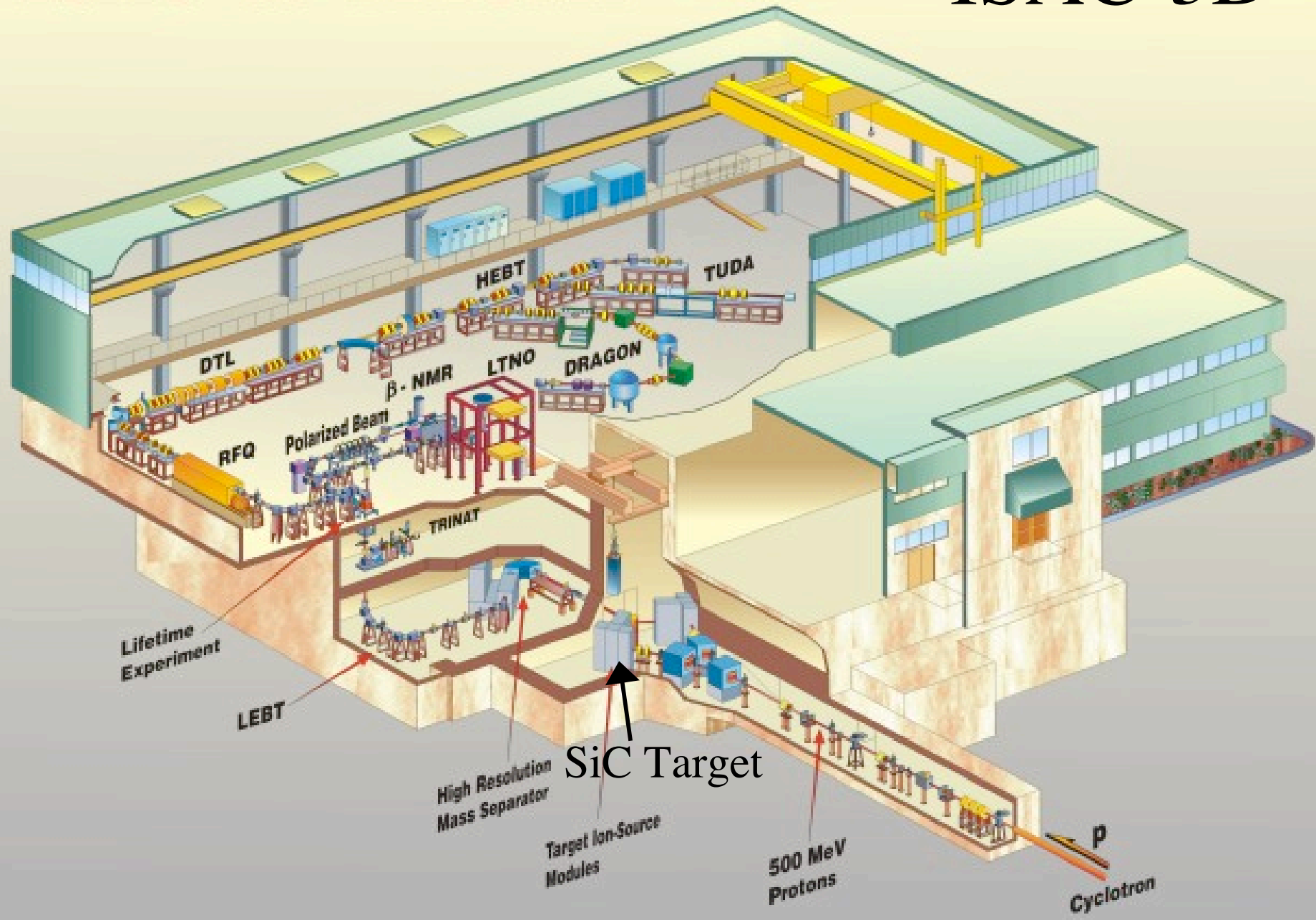
Li, B 不純物によるドナー／アクセプター準位形成？



$$\propto \exp(-E_a/kT)$$

ISAC at TRIUMF

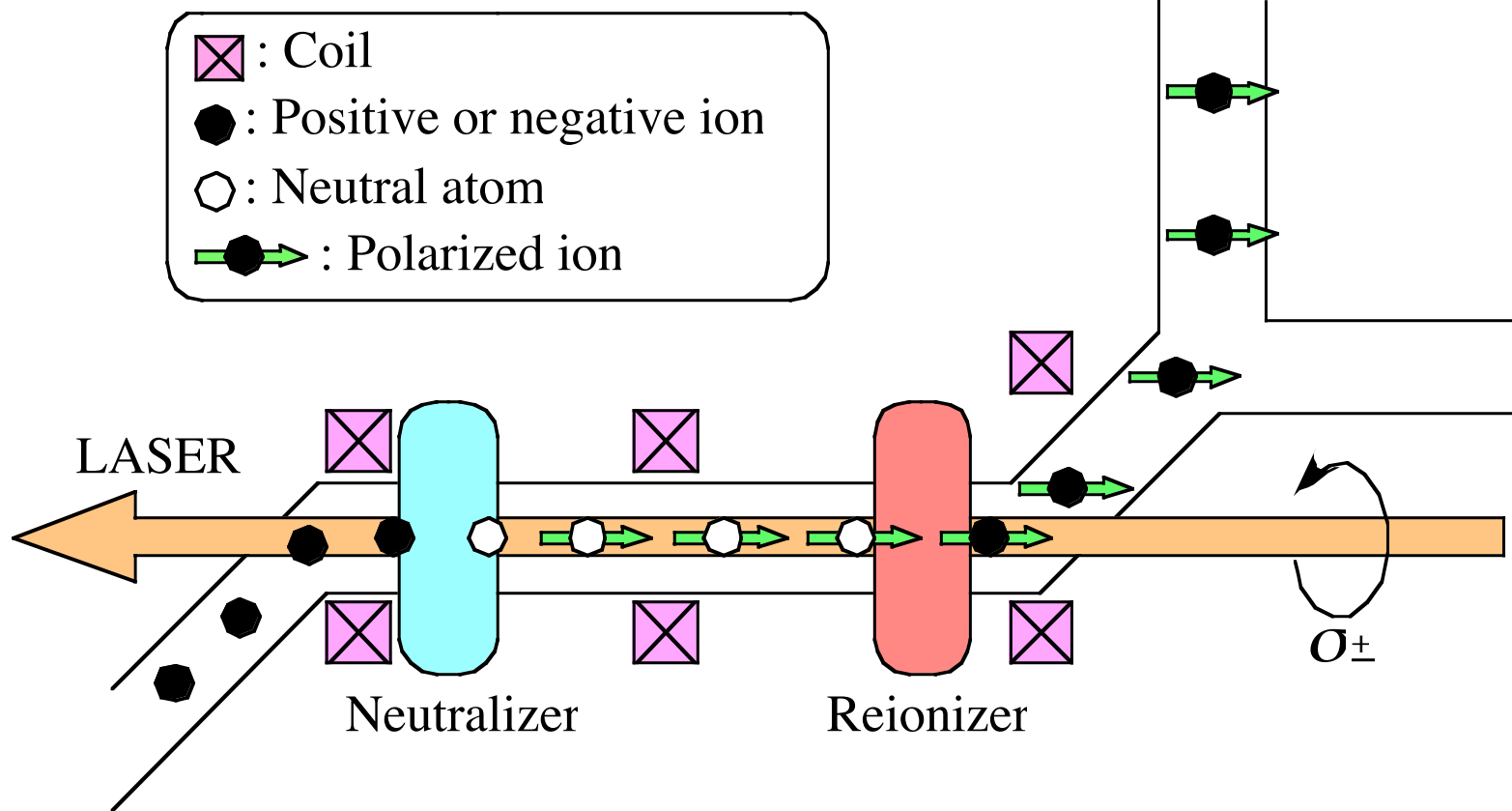
ISAC-3D



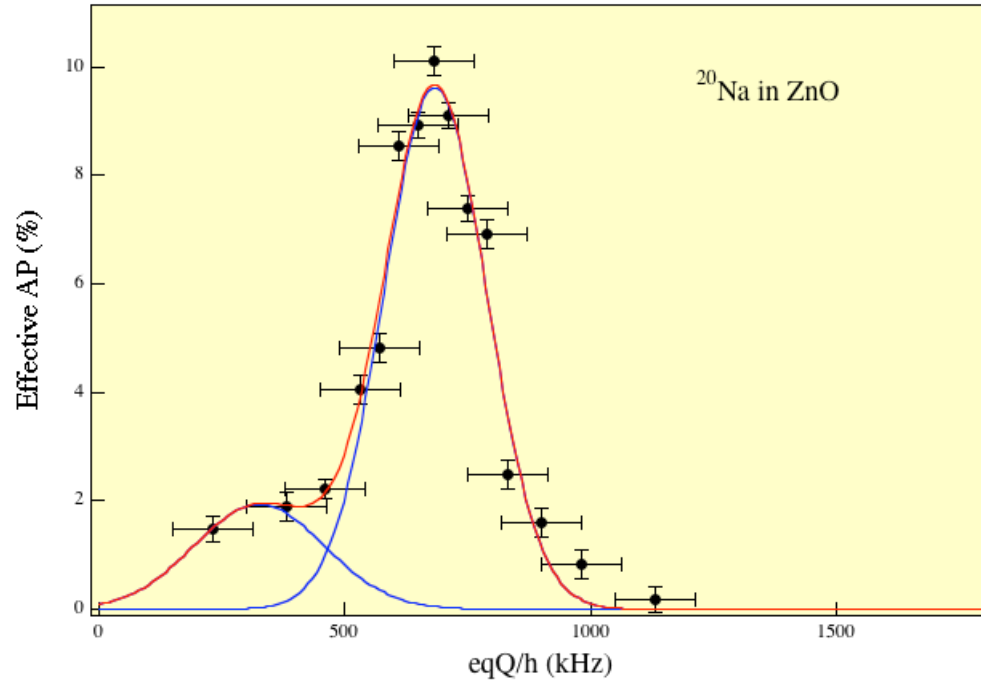
Polarizer beam line

TRIUMF/ISAC Polarizer Beamline

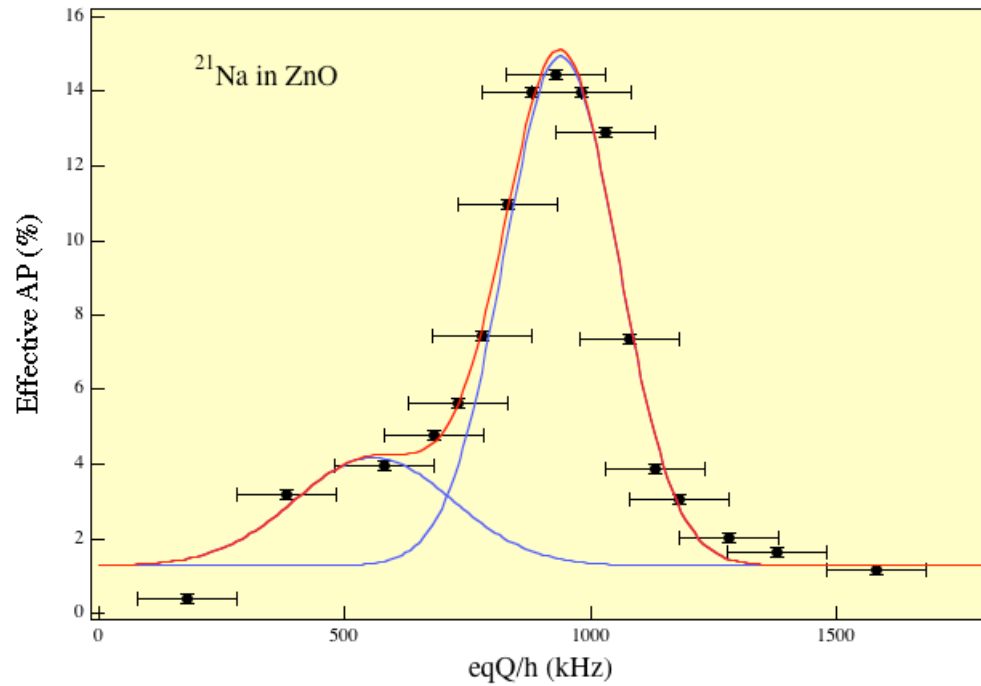
OSAKA II
Exp. port



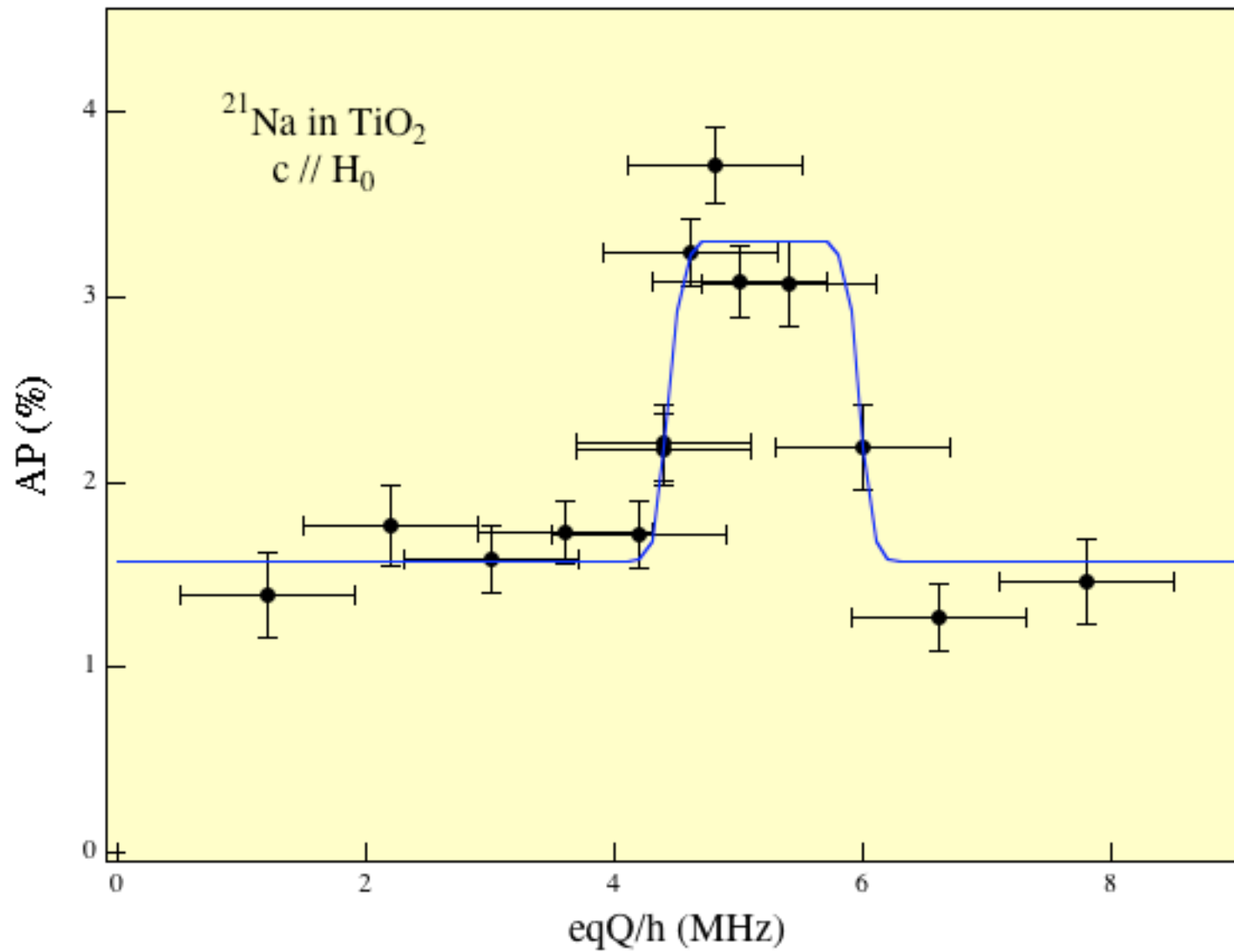
^{20}Na in ZnO



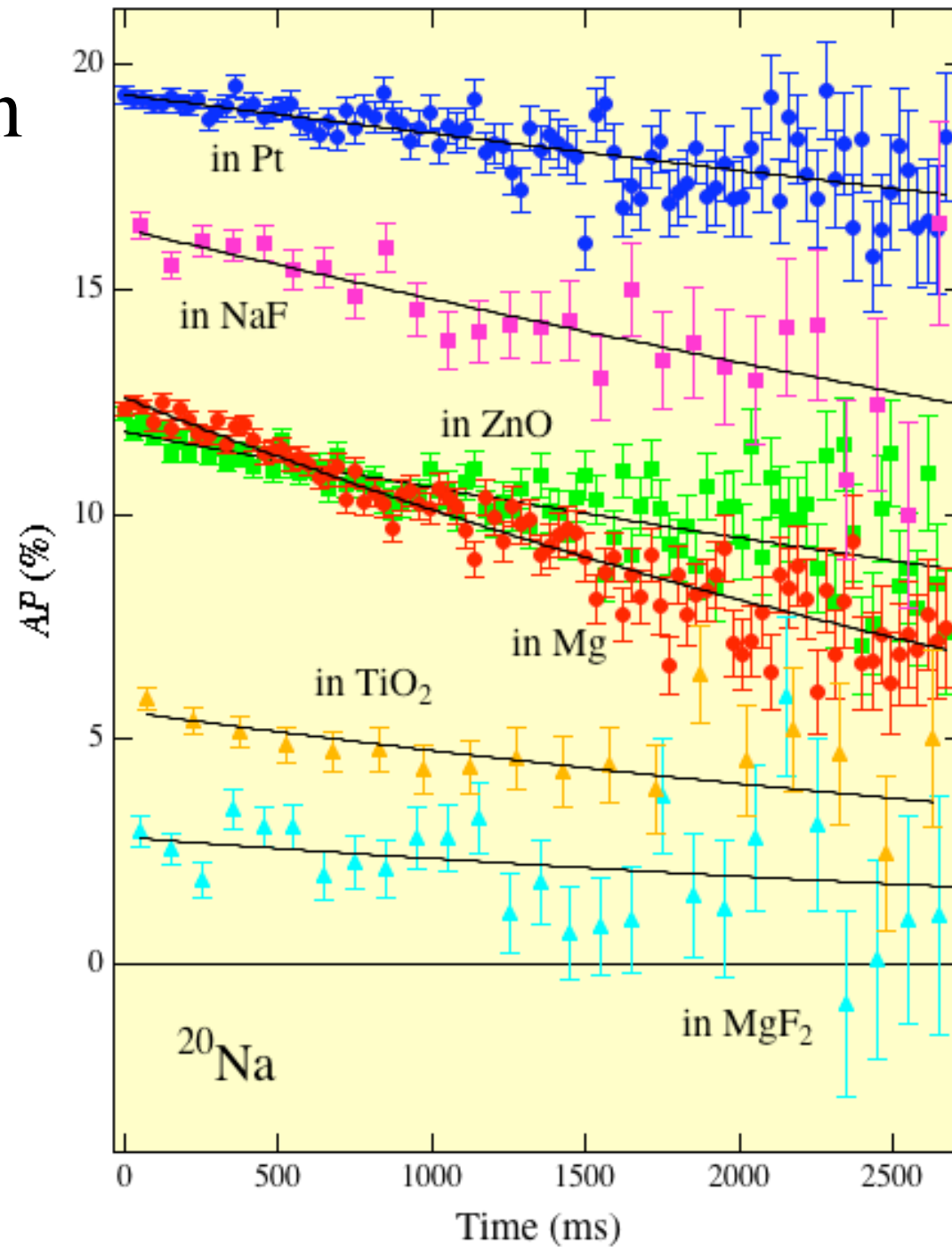
^{21}Na in ZnO



^{21}Na in TiO_2



Polarization relaxation



Relaxation ^{25}Na in TiO_2 @HIMAC

