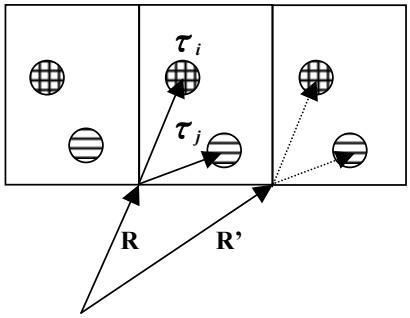
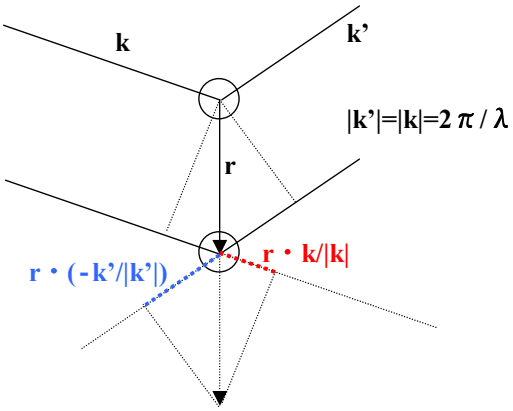




1 Lattice and basis

・ The structure of all crystal can be described in terms of lattice, with a group of atoms attached to every lattice point. The group of atoms is called the basis.

crystal structure = **lattice** {**R**} **+ basis** {τ}

A lattice translation vector can be described by the primitive cell vectors （基本単位格子ベクトル）

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{1}$$

2 Optical path length, Superposition of waves: diatomic and lattice system

・The difference of the optical path length(光路差) for two atom scatteirng is given by $\Delta = \mathbf{k}/|\mathbf{k}|\cdot\mathbf{r} - \mathbf{k}'/|\mathbf{k}'|\cdot\mathbf{r}$. If the detector is located at $\mathbf{r}'$, ($r' >> r$　すなわち, 球面波は遠方で平面波とみなせる。）the superposition of the electromagnetic wave ψ_1 and ψ_2 is given by ($e^{ix} = \cos x + i\sin x$) (光路差を波長で割ったもの $\times 2\pi$ が波の位相 $(kx - \omega t)$ に入ってくる。)

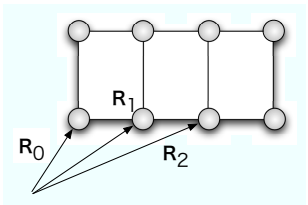
$$\begin{aligned}
\Psi &= \psi_1 + \psi_2 = \exp[i(\mathbf{k}'\cdot\mathbf{r}' - \omega t)] + \exp[i(\mathbf{k}'\cdot\mathbf{r}' + 2\pi\frac{\Delta}{\lambda} - \omega t)] = \exp[i(\mathbf{k}'\cdot\mathbf{r}' - \omega t)][1 + \exp(2\pi i\frac{\Delta}{\lambda})] && (2)\\
&= \exp[i(\mathbf{k}'\cdot\mathbf{r}' - \omega t)][1 + \exp(i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r})] && (3)\\
\Delta &= \mathbf{k}/|\mathbf{k}|\cdot\mathbf{r} - \mathbf{k}'/|\mathbf{k}'|\cdot\mathbf{r} = \frac{\lambda}{2\pi}(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r} && (4)
\end{aligned}$$

(2) 式より，Δ が波長の整数倍の時波は強め合い，Δ が波長の半整数倍の時波は消しあう。

$$\Delta = \frac{\mathbf{k}}{|\mathbf{k}|}\cdot\mathbf{r} - \frac{\mathbf{k}'}{|\mathbf{k}'|}\cdot\mathbf{r} = n\lambda, \quad \mathbf{k} \equiv \frac{2\pi}{\lambda}\frac{\mathbf{k}}{|\mathbf{k}|}, \quad |\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda} \quad (elastic scattering) \tag{5}$$

$$\begin{aligned}
(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r} &= n\lambda\frac{2\pi}{\lambda}\\
&= 2\pi n && (6)\\
(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r} &= 2\pi\frac{\text{optical path diffrence}}{\lambda} && (7)
\end{aligned}$$

Here we will replace **r** by {$\mathbf{R}_i$ }, i.e. we consider the lattice system without basis. Ψ becomes



$$\begin{aligned}
\Psi &= \sum_{\mathbf{R}_i}\psi_i = \exp[i(\mathbf{k}'\cdot\mathbf{r}' - \omega t)][1 + \exp(2\pi i\frac{\Delta_1}{\lambda}) + \exp(2\pi i\frac{\Delta_2}{\lambda}) + ...] && (8)\\
\Delta_i &= (\frac{\mathbf{k}}{|\mathbf{k}|} - \frac{\mathbf{k}'}{|\mathbf{k}'|})\cdot(\mathbf{R}_i - \mathbf{R}_0) && (9)
\end{aligned}$$

全ての格子点からの散乱が強め合うのは，$\Delta_i = n\lambda$ の時であり，従って，$\mathbf{R}_0 = 0$ とすれば

$$(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_i = 2\pi n \tag{10}$$

となる。この関係を満たす $\mathbf{G}(= \mathbf{k} - \mathbf{k}')$ は逆格子 (**reciprocal lattice**) よばれる。以下では，逆格子の性質について考えよう。

3 Reciprocal Lattice, Miller Index, Laue Condition

・ Any function invariant under a lattice translation $\mathbf{R}$ may be expanded in a Fourier series of the form [1] [2]

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \tag{21}$$

$$n(\mathbf{r} + \mathbf{R}) = n(\mathbf{r}) \tag{22}$$

$$\exp(i\mathbf{G} \cdot \mathbf{R}) = 1 \tag{23}$$

・ If we define the reciprocal lattice $\mathbf{b}_j$(逆格子)

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \tag{24}$$

The primitive translation vectors of the reciprocal lattice are

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \tag{25}$$

Here $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the primitive translation vectors of the crystal lattice.

Example: simple cubic lattice (単純立方格子)

$$\begin{aligned} \mathbf{a}_1 &= (a, 0, 0), \quad \mathbf{a}_2 = (0, a, 0), \quad \mathbf{a}_3 = (0, 0, a) \\ \mathbf{b}_1 &= (b, 0, 0), \quad \mathbf{b}_2 = (0, b, 0), \quad \mathbf{b}_3 = (0, 0, b) \\ b &= \frac{2\pi}{a} \end{aligned}$$

・ A reciprocal lattice vector has the form

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, \tag{26}$$

where h, k, l are integers or zero. This equation satisfies $\exp(i\mathbf{G} \cdot \mathbf{R}) = 1$.

If we consider $\mathbf{a}_1/h, \mathbf{a}_2/k, \mathbf{a}_3/l$ plane (hkl Miller index:ミラー指数), the reciprocal lattice vector $\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is perpendicular to this plane. The distance between the two adjacent parallel planes of the lattice is $d(hkl) = 2\pi/|\mathbf{G}_{hkl}|$.

[1]

$$n(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}}\int_{\text{cell}} d\mathbf{r} n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} \left(= \frac{1}{\Omega}\int d\mathbf{r} n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}\right) \tag{11}$$

$$= \sum_{\mathbf{G}'} n(\mathbf{G}') \frac{1}{\Omega_{\text{cell}}} \underbrace{\int_{\text{cell}} d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}}}_{\delta_{\mathbf{G}',\mathbf{G}}\Omega_{\text{cell}}} = n(\mathbf{G}) \tag{12}$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}} \underbrace{\frac{1}{\Omega_{\text{cell}}}\int_{\text{cell}} d\mathbf{r}' n(\mathbf{r}') e^{-i\mathbf{G}\cdot\mathbf{r}'}}_{n(\mathbf{G})} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{13}$$

$$= \frac{1}{N_{\text{cell}}}\int d\mathbf{r}' n(\mathbf{r}') \frac{1}{\Omega_{\text{cell}}} \underbrace{\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')}}_{\Omega\delta_{\mathbf{r},\mathbf{r}'}} = n(\mathbf{r}) \tag{14}$$

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')} = \frac{1}{\Delta G_x \Delta G_y \Delta G_z}\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')}\Delta G_x \Delta G_y \Delta G_z = \frac{\Omega}{8\pi^3}\int d\mathbf{G} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')} = \frac{8\pi^3\Omega}{8\pi^3}\delta(\mathbf{r} - \mathbf{r}') \tag{15}$$

[2] フーリエ級数、フーリエ変換　(フーリエの冒険という本がわかりやすい。) 関数 $f(x)$ が $[-l, l]$ の繰り返し周期 $2l$ をもつとき、関数は以下のように展開できる

$$f(x) \sim \sum_{n=-\infty}^{n=\infty} c_n \mathrm{e}^{in\pi x/l} \tag{16}$$

ただし、

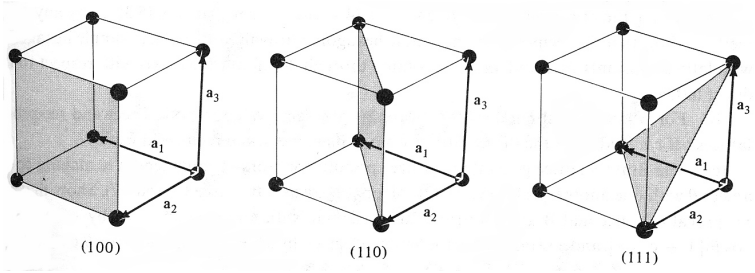
$$c_n = \frac{1}{2l}\int_{-l}^{l} dx f(x) \mathrm{e}^{-in\pi x/l} \tag{17}$$

周期 l が無限大の時、級数は連続数 $k_n \equiv n\pi/l$ は連続数 k になり, $\Delta_n = \pi/l$ とすると

$$f(x) = \lim_{l\to\infty}\frac{1}{\Delta_n}\sum_{n=-\infty}^{n=\infty} c_n \mathrm{e}^{in\pi x/l}\Delta_n \tag{18}$$

$$= \int_{-\infty}^{\infty} dk c(k) e^{ikx} \tag{19}$$

$$c(k) \equiv \frac{c_n}{\Delta_n} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx f(x) \mathrm{e}^{-ikx} \tag{20}$$



proof: An arbitary vector $\mathbf{t}$ in the (hkl) plane can be described

$$\mathbf{t} = \alpha(\mathbf{a}_1/h - \mathbf{a}_2/k) + \beta(\mathbf{a}_2/k - \mathbf{a}_3/l) \tag{27}$$

The inner product

$$\begin{aligned} \mathbf{G}_{hkl} \cdot \mathbf{t} &= 2\pi\alpha(h/h - k/k) + 2\pi\beta(k/k - l/l) \\ &= 0 \end{aligned} \tag{28}$$

Thereby $\mathbf{G}_{hkl}$ is perpendicular to the (hkl) plane. If we define the vector $\mathbf{d}$ is the one from the origin to the intersection of (hkl) plane and the vector $\mathbf{G}$

$$\begin{aligned} \mathbf{d} &= \frac{\mathbf{G}_{hkl}}{|\mathbf{G}_{hkl}|} d(hkl) \\ \frac{\mathbf{G}_{hkl}}{|\mathbf{G}_{hkl}|} \cdot \mathbf{d} &= d(hkl) \\ \mathbf{d} &= \frac{\mathbf{a}_1}{h} + \mathbf{t}_{\text{intersect}} \\ \mathbf{G}_{hkl} \cdot \mathbf{d} &= \frac{\mathbf{G}_{hkl} \cdot \mathbf{a}_1}{h} + \mathbf{G}_{hkl} \cdot \mathbf{t}_{\text{intersect}} \\ &= \frac{2\pi h}{h} + 0 = 2\pi \qquad \text{then} \\ d(hkl) &= \frac{2\pi}{|\mathbf{G}_{hkl}|} \end{aligned} \tag{29}$$

・The difference of the optical path length from crystal (結晶内での光路差)　If we replace $\mathbf{r}$ in Eqs.(2) and (3) by $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

$$(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R} = 2\pi n \tag{30}$$

From the above equaitions, then we can get **Laue condition**

$$\mathbf{k}' - \mathbf{k}(\equiv \Delta\mathbf{k}) = \mathbf{G} \tag{31}$$

・ Various statements of the Bragg condition:

$$\mathbf{k}' = \mathbf{k} + \mathbf{G} \tag{32}$$

$$k'^2 = k^2 + 2\mathbf{k} \cdot \mathbf{G} + G^2 \tag{33}$$

$$2\mathbf{k} \cdot \mathbf{G} = -G^2 \tag{34}$$

$$2\frac{2\pi}{\lambda} G \cos(\pi/2 + \theta) = -G^2 \tag{35}$$

$$2\frac{2\pi}{\lambda} \sin\theta = G \tag{36}$$

$$2\frac{2\pi}{\lambda} \sin\theta = 2\pi/d(hkl) \tag{37}$$

$$2d(hkl) \sin\theta = \lambda \tag{38}$$

$$2d \sin\theta = n\lambda; \quad \Delta\mathbf{k} = \mathbf{G}; \quad 2\mathbf{k} \cdot \mathbf{G} = -\mathbf{G}^2. \tag{39}$$

・ Laue conditions:

$$\mathbf{a}_1 \cdot \Delta\mathbf{k} = 2\pi v_1; \quad \mathbf{a}_2 \cdot \Delta\mathbf{k} = 2\pi v_2; \quad \mathbf{a}_3 \cdot \Delta\mathbf{k} = 2\pi v_3 \tag{40}$$

4 Structure factor, Atomic Form Factor

一般の結晶の場合を考えよう。結晶の周期性をもつ電子の密度を $n(\mathbf{r})$ とすると，波の重ね合わせは，

$$\Psi = \exp[i(\mathbf{k}' \cdot \mathbf{r}' - \omega t)] \sum n(\mathbf{r}_i) \exp(2\pi i \Delta(\mathbf{r}_i)/\lambda) \tag{41}$$

和を積分にすると，・ The amplitude of the scattered wave in the direction of $\mathbf{k}'$ is proportional to the integral over the crystal of $n(\mathbf{r})dV$ times the phase factor $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$.

$$
\begin{aligned}
F &= \int dV n(\mathbf{r}) \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}] && (42)\\
&= N_{\text{cell}} \int_{\text{cell}} dV n(\mathbf{r}) \exp(-i\mathbf{G}\cdot\mathbf{r}) && (43)\\
&= N_{\text{cell}} S_{\mathbf{G}} && (44)
\end{aligned}
$$

２番目の式で，格子の周期性と Laue condition を使った。The $S_{\mathbf{G}}$ is called **structure factor（構造因子）**. If we consider the basis

$$
n(\mathbf{r}) = \sum_{j=1}^{s} n_j(\mathbf{r}-\tau_j) \tag{45}
$$

$$
\begin{aligned}
S_{\mathbf{G}} &= \sum_j \int_{\text{cell}} dV n_j(\mathbf{r}-\tau_j) \exp(-i\mathbf{G}\cdot\mathbf{r}) && (46)\\
&= \sum_j \exp(-i\mathbf{G}\cdot\tau_j) \int_{\text{cell}} dV' n_j(\mathbf{r}') \exp(-i\mathbf{G}\cdot\mathbf{r}'), \qquad \mathbf{r}' = \mathbf{r}-\tau_j && (47)\\
&= \sum_j f_j \exp(-i\mathbf{G}\cdot\tau_j) && (48)\\
f_j &\equiv \int_{\text{cell}} dV' n_j(\mathbf{r}') \exp(-i\mathbf{G}\cdot\mathbf{r}') && (49)\\
& && (50)
\end{aligned}
$$

f_j has an atomic property and is called atomic form factor. If the basis vectors are described in the primitive lattice unit

$$
\tau_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3, \qquad 0 \le x_j, y_j, z_j \le 1 \tag{51}
$$

$$
S_{\mathbf{G}}(hkl) = \sum f_j \exp(-i\mathbf{G}\cdot\tau_j) = \sum f_j \exp[-i2\pi(hx_j + ky_j + lz_j)] \tag{52}
$$

where j runs over the s atoms of the basis, and f_j is the **atomic form factor（原子散乱因子）** of the jth atom of the basis. The expression on the right-hand side is written for a reflection (h,k,l) for which $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.

5 Phase Problem

The structure factor S need not be real because the scattered intensity I_{hkl} is given by $S^*_{\mathbf{G}_{hkl}} S_{\mathbf{G}_{hkl}}$. In the XRD measurements the scattered intensity can be observed, not for the structure factor.

$$
\begin{aligned}
I &\propto |S_{\mathbf{G}}|^2 && (53)\\
& && (54)
\end{aligned}
$$

Final goal is to get the structure(or electron denisty map) [3]

$$
n(\mathbf{r}) = \frac{1}{\Omega_{\text{cell}}} \sum_{\mathbf{G}_{hkl}} S(\mathbf{G}_{hkl}) e^{i\mathbf{G}_{hkl}\cdot\mathbf{r}} \tag{55}
$$

$S(\mathbf{G}_{hkl})$ is the imaginary quantity and we can write

$$
S(\mathbf{G}_{hkl}) = |S(\mathbf{G}_{hkl})| e^{i\phi_{\mathbf{G}_{hkl}}} \tag{56}
$$

From the diffraction intensities we can get $|S(\mathbf{G}_{hkl})|$ but not the phase（位相） $\phi_{\mathbf{G}_{hkl}}$ People call this ”Phase problem” and there are some method to solve it.

[3]

$$
\begin{aligned}
\frac{1}{\Omega_{\text{cell}}} \sum_{\mathbf{G}} S(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} &= \frac{1}{\Omega_{\text{cell}}} \sum_j \int_{\text{cell}} dV' n_j(\mathbf{r}'-\tau_j) \sum_{\mathbf{G}} \exp[i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')] = \frac{1}{\Omega_{\text{cell}}} \sum_j \int_{\text{cell}} dV' n_j(\mathbf{r}'-\tau_j) \Omega\delta(\mathbf{r}-\mathbf{r}')\\
&= \frac{\Omega}{N_{\text{cell}}\Omega_{\text{cell}}} \sum_j \int dV' n_j(\mathbf{r}'-\tau_j)\delta(\mathbf{r}-\mathbf{r}') = \sum_j n_j(\mathbf{r}-\tau_j) = n(\mathbf{r})
\end{aligned}
$$

Let's consider an example. Here the system has inversion symmetry $n(\mathbf{r}) = n(-\mathbf{r})$.

$$\begin{aligned}\sum_{\mathbf{G}} S(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} &= \sum_{\mathbf{G}} S(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} = \sum_{\mathbf{G}'(=-\mathbf{G})} S(-\mathbf{G}') e^{i\mathbf{G}'\cdot\mathbf{r}} \\ S(\mathbf{G}) &= S(-\mathbf{G})\end{aligned}$$

The electron density should be real, then $n(\mathbf{r}) = n^*(\mathbf{r})$ From $n(-\mathbf{r}) = n^*(\mathbf{r})$

$$\begin{aligned}\sum_{\mathbf{G}} S(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} &= \sum_{\mathbf{G}} S^*(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} \\ S(\mathbf{G}) &= S^*(\mathbf{G}), \quad (S(\mathbf{G}) \text{ is real.})\end{aligned}$$

The electron density become

$$\Omega_{\text{cell}} n(\mathbf{r}) = S(0) + \sum_{\mathbf{G}>0} 2S(\mathbf{G}) \cos(\mathbf{G}\cdot\mathbf{r})$$

We also assume that the electron denisty depend on z-direction only, and the density can be described by $\mathbf{G}_{00k}, k \leqslant 3$ in $\mathbf{k}$-space.

$$\begin{aligned}\Omega_{\text{cell}} n(z) &= S(0) + 2S(\mathbf{G}_{001}) \cos(\mathbf{G}_{001}\cdot\mathbf{r}) + 2S(\mathbf{G}_{002}) \cos(\mathbf{G}_{002}\cdot\mathbf{r}) + 2S(\mathbf{G}_{003}) \cos(\mathbf{G}_{003}\cdot\mathbf{r}) \\ &= S(0) + 2S(\mathbf{G}_{001}) \cos(\frac{2\pi}{a}z) + 2S(\mathbf{G}_{002}) \cos(\frac{4\pi}{a}z) + 2S(\mathbf{G}_{003}) \cos(\frac{6\pi}{a}z), \quad (\mathbf{G}_{001} = \frac{2\pi}{a}\hat{\mathbf{z}})\end{aligned}$$

For example, we got $S(0) = 3.0, |S(\mathbf{G}_{001})| = 0.5, |S(\mathbf{G}_{002})| = 0.5, |S(\mathbf{G}_{003})| = 0.5$ from XRD measurments. From $S(\mathbf{G}) = |S(\mathbf{G})| e^{i\phi(\mathbf{G})}$ and $S(\mathbf{G})$ is real, then

$$\phi(\mathbf{G}) = 0, \quad \pi$$

Then we should consider eight cases $S(0) = 3.0, S(\mathbf{G}_{001}) = \pm 0.5, S(\mathbf{G}_{002}) = \pm 0.5, S(\mathbf{G}_{003}) = \pm 0.5$. In the following figure the electron denisty profiles are shown. **Please note that the density profiles are not the same for all eight caes!!（全部のプロファイルが異なる。!!）** この問題は，一般にはあまり重要にはとらえられていないが，散乱強度の実験から構造等を得る時に大変重大な問題となる。The anomalous dispersion of atomic form factor at the absorption edge is used to solve this phase problem. 9 章に解説を付け加えた。（Please find the them in the book, e,g, "大場矢野, X 線構造解析, 日本化学会, 朝倉, 1999")

6 Structure factor: Example

・example:fcc ：basis at $000; 0(1/2)(1/2); (1/2)0(1/2); (1/2)(1/2)0$

$$S(hkl) = f\{1 + \exp[-i\pi(k+l)] + \exp[-i\pi(h+l)] + \exp[-i\pi(h+k)]\} \tag{57}$$

hkl: all even $S = 4f$
hkl: all odd $S = 4f$
hkl: one is even and other two are odd $S = 0$
・Atomic Form Factor
If the electron distribution of the basis j is spherical

$$f_j = 4\pi \int dr n_j(r) r^2 \frac{\sin Gr}{Gr} \tag{58}$$

$$\lim_{G\to 0} f_j = Z(= \text{atomic number}) \tag{59}$$

・Quiz1
KCl and KBr (both NaCl type)
K^+:$000; 0(1/2)(1/2); (1/2)0(1/2); (1/2)(1/2)0$ Cl^-, Br^-: $(1/2)00; (1/2)(1/2)(1/2); 00(1/2); 0(1/2)0$

$$\begin{aligned}S_{\mathbf{G}_{hkl}} &= f_{K^+}(1 + e^{-i\pi(k+l)} + e^{-i\pi(h+l)} + e^{-i\pi(h+k)}) \\ &\quad + f_{Cl^-}(e^{-i\pi h} + e^{-i\pi(h+k+l)} + e^{-i\pi l} + e^{-i\pi k})\end{aligned} \tag{60}$$

For (111) plane $S_{111} = 4f_{K^+} - 4f_{Cl^-}$, and for (200) plane $S_{200} = 4f_{K^+} + 4f_{Cl^-}$. If we consider $Z(\text{K}) = 19, Z(\text{Cl}) = 17, Z(\text{Br}) = 35$, the (111) peak for KCl cannot be observed.

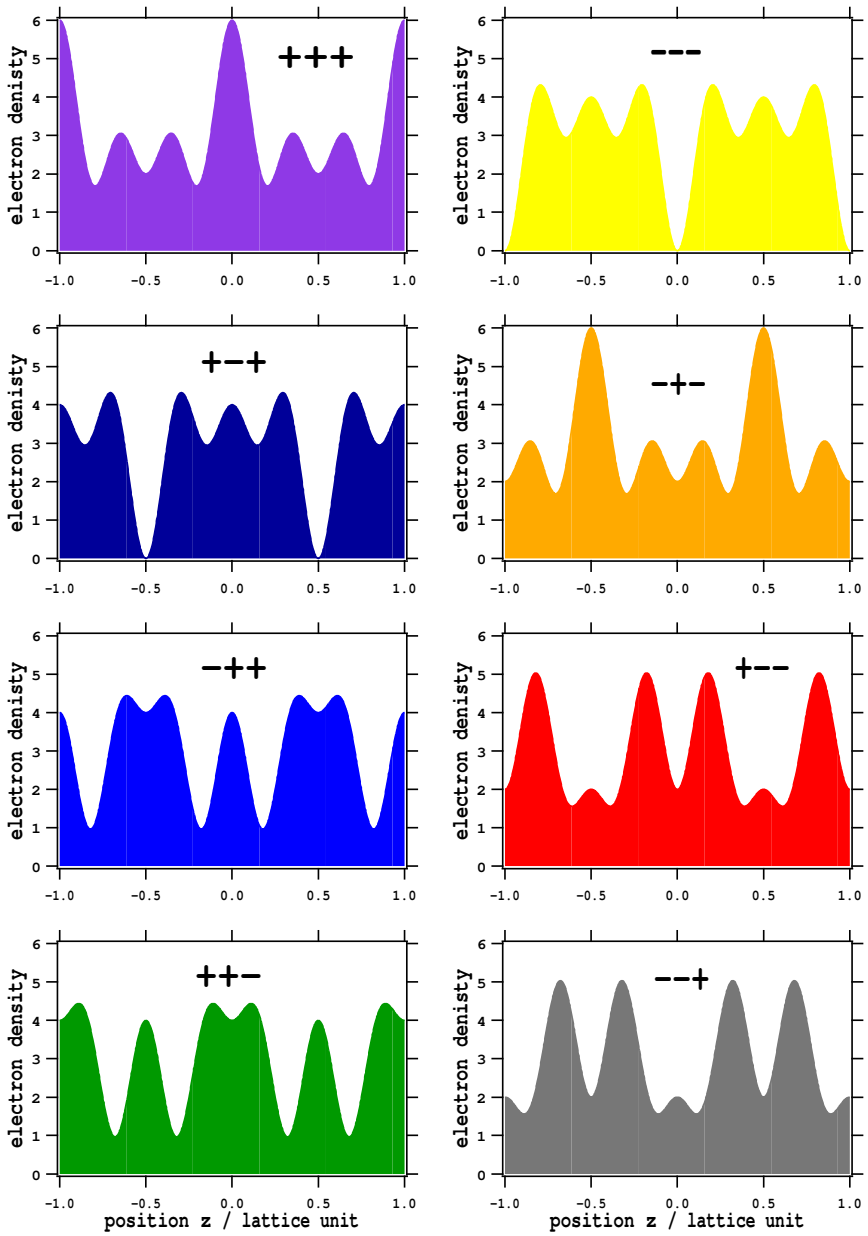


Figure 1: Electron denisty profile for the structure factor $S(0) = 3.0, S(\mathbf{G}_{001}) = \pm 0.5, S(\mathbf{G}_{002}) = \pm 0.5, S(\mathbf{G}_{003}) = \pm 0.5$.

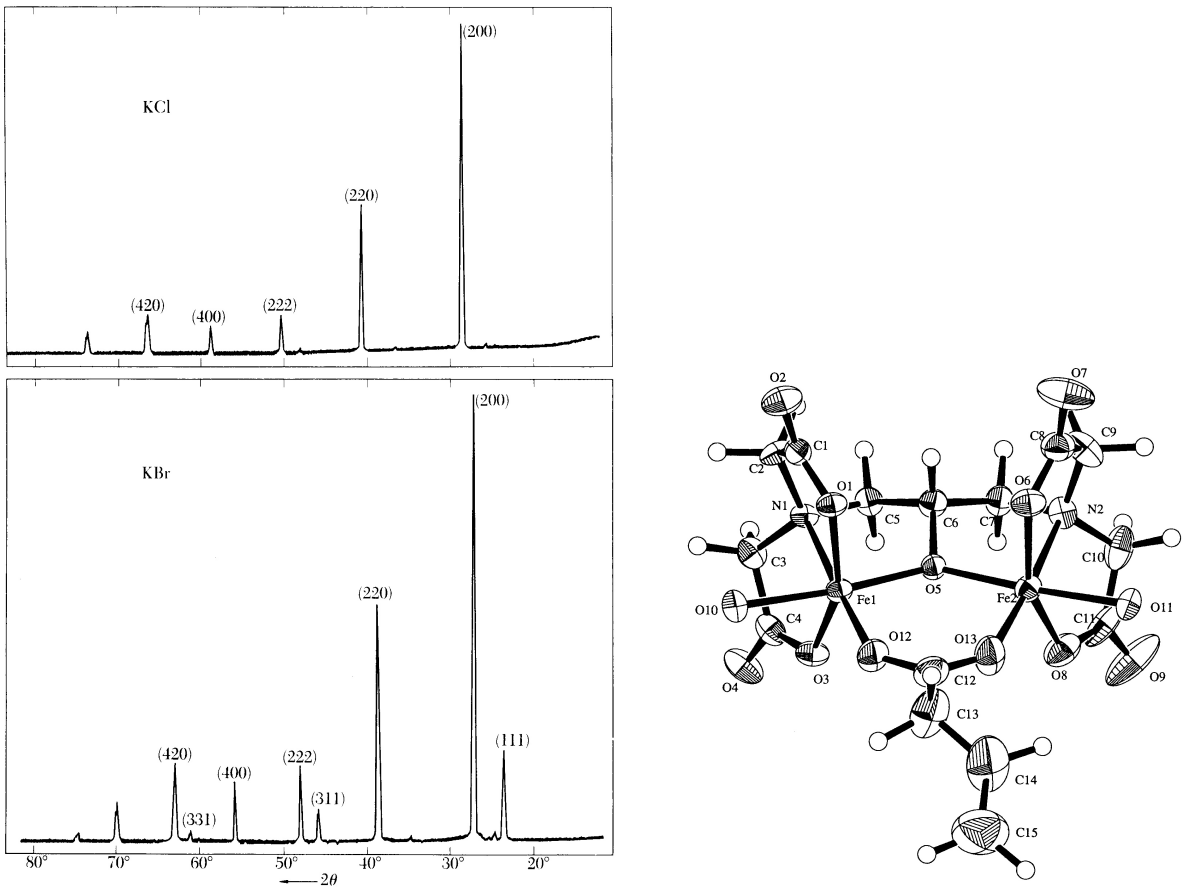
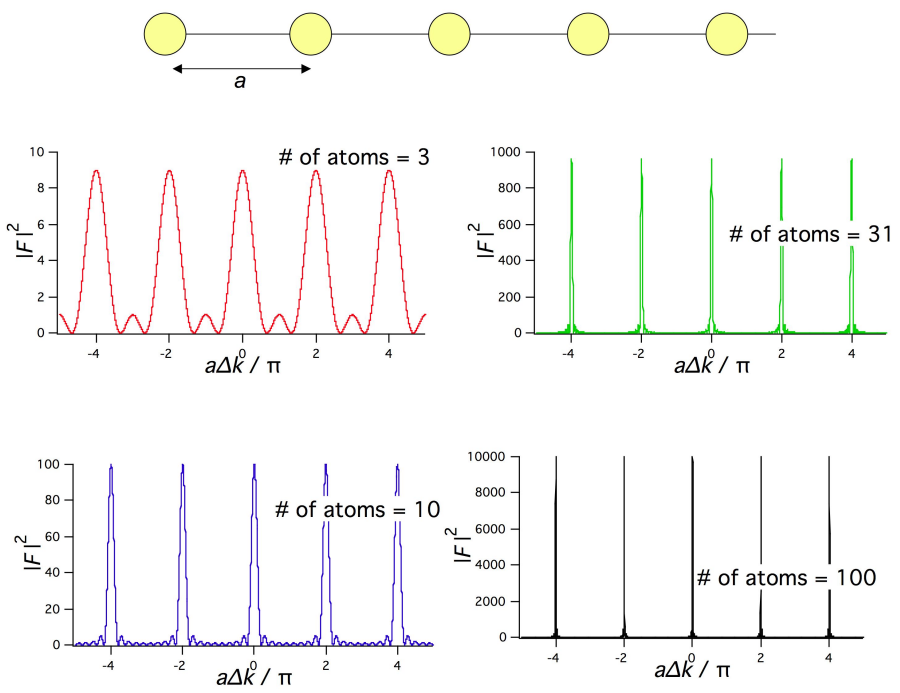


Figure 2: Powder XRD pattern for KCl and KBr(left) ORTEP (Oak Ridge Thermal Ellipsoid Plot)(right)



7 Peak Width

・Quiz2　十分な回折光を得るには何原子必要か？　1 次元モデルで説明せよ。（キーワード：回折ピーク幅）

$$
\begin{aligned}
n(x) &= \sum_{m=0}^{M-1} \delta(x - ma) \\
F(\Delta k) &= \int dx n(x) \exp[i(\Delta k)x] \\
&= \sum_{m=0}^{M-1} \exp[i(\Delta k)ma] \\
&= \frac{1 - \exp(-iMa\Delta k)}{1 - \exp(-ia\Delta k)} \\
|F|^2 &\equiv F^*F = \frac{1 - \exp(iMa\Delta k)}{1 - \exp(ia\Delta k)} \frac{1 - \exp(-iMa\Delta k)}{1 - \exp(-ia\Delta k)} \\
&= \frac{2 - 2\cos(Ma\Delta k)}{2 - 2\cos(a\Delta k)}
\end{aligned}
$$

$$
\begin{aligned}
a\Delta k &\to 0 \\
\cos(a\Delta k) &\simeq 1 - \frac{(a\Delta k)^2}{2} \\
\cos(Ma\Delta k) &\simeq 1 - \frac{M^2(a\Delta k)^2}{2} \\
|F|^2 &\simeq \frac{2 - 2(1 - \frac{M^2(a\Delta k)^2}{2})}{2 - 2(1 - \frac{(a\Delta k)^2}{2})} = M^2
\end{aligned}
$$

PHYSICAL REVIEW B 72, 195402 (2005)

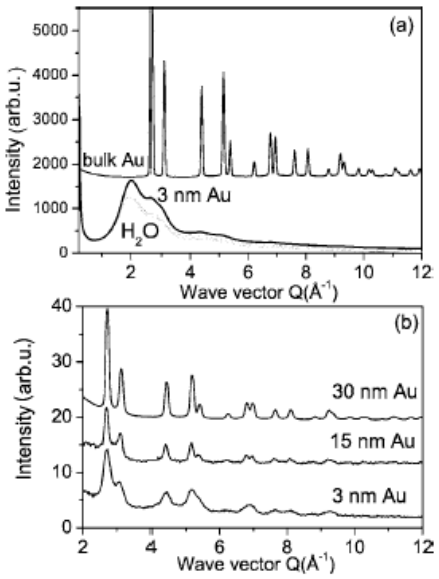


FIG. 3. (a) X-ray diffraction patterns for water (symbols), 3 nm Au nanoparticles in water and bulk gold (solid lines). (b) X-ray diffraction patterns for 3 nm, 15 nm, and 30 nm Au nanoparticles corrected for water and background scattering.

8 Debye-Waller Factor

Quiz3　温度を上げるとどうなる？(keyword:Debye-Waller 因子)

格子振動を各原子は独立に調和振動するという Einstein model を考える。

$$\mathbf{r}_j(t) = \mathbf{r}_j^0 + \mathbf{u}_j(t) \tag{61}$$

$$I(hkl) = I_0 \exp(-\frac{1}{3}\langle u^2\rangle G^2), \quad \frac{1}{2}M\omega^2\langle u^2\rangle = \frac{3}{2}k_BT \quad \text{(Einstein model)} \tag{62}$$

$$I(hkl) = I_0 \exp(-\frac{k_BTG_{hkl}^2}{M\omega^2}) \tag{63}$$

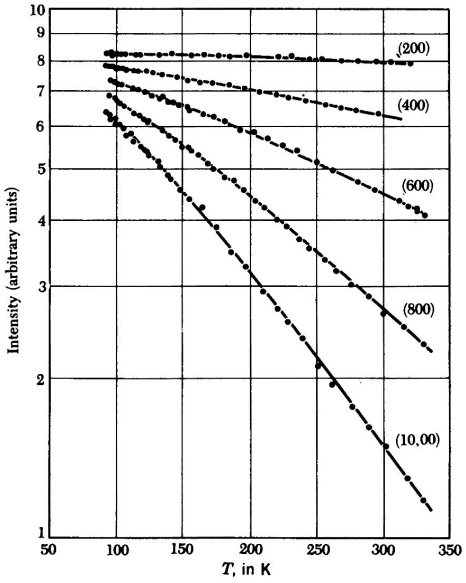


Figure 1 The dependence of intensity on temperature for the (h00) x-ray reflections ot aluminum. Reflections (h00) with h odd are forbidden for an fcc structure. (After R. M. Nicklow and R. A. Young.)

温度が高いほど，G_{hkl} が大きいほど，系がソフト (ω small) なほど強度の減衰は大きい。

9 原子散乱因子の異常分散と位相問題

Atomic form factor becomes imaginary around the absorption edge.

$$\begin{aligned} f &= \mathrm{Re}f + i\mathrm{Im}f \\ \mathrm{Re}f &= f_0 + f' + f_{\mathrm{NT}}, \quad f' = f_1 + f_{\mathrm{rel}} - Z \\ f_0 &= 4\pi \int drn(r)r^2 \frac{\sin Gr}{Gr} \\ \mathrm{Im}f &= f_2 \end{aligned}$$

Here we define the anomalous scattering factor:f', the small nuclear Thomson term: f_{NT}, the small relativistic correction term f_{rel}, f_2 is related to the absorption. In the followinf figures, f_1 and f_2 for Se atom are shown. We can write

$$f = f_0 + f'(E) + if''(E) \tag{64}$$

Now we assume that the crystal has one component of atom which has the anomalous form factor. In the structure factor we can separate the atoms which has anomalous form factor.(Hendrickson)

$$S_{\mathbf{G}} = \sum f_j \exp(-i\mathbf{G}\cdot\tau_j) \tag{65}$$

$$= \sum f_{0,j} \exp(-i\mathbf{G}\cdot\tau_j) + \sum_{k\in\text{anomal}} [f_{k,0} + f_k'(E) + if_k''(E)] \exp(-i\mathbf{G}\cdot\tau_k) \tag{66}$$

$$f_{k,0} + f_k'(E) + if_k''(E) = f_{0,A} + f_A'(E) + if_A''(E) \tag{67}$$

$$S_{\mathbf{G}} = \sum_j f_{0,j} \exp(-i\mathbf{G}\cdot\tau_j) + (1 + \frac{f_A'(E) + if_A''(E)}{f_{0,A}}) \sum_{k\in\text{anomal}} f_{0,A} \exp(-i\mathbf{G}\cdot\tau_k) \tag{68}$$

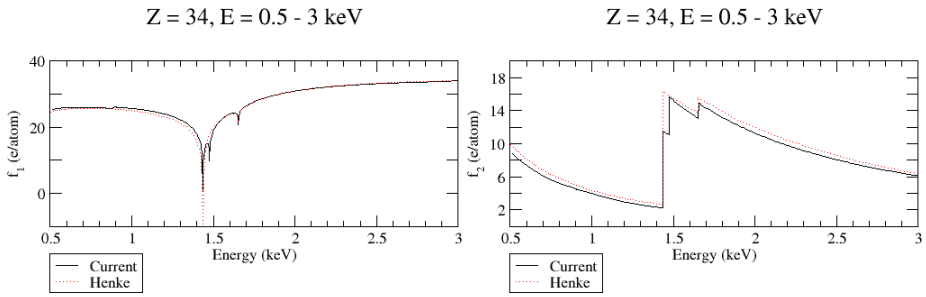


Figure 3: energy dependence of the atomic form factor for Se atom. NIST X-Ray Form Factor, Atten., and Scattering Database

$$= \sum_{j,\text{all}} f_{0,j}\exp(-i\mathbf{G}\cdot\tau_j) + \frac{f'_A(E)+if''_A(E)}{f_{0,A}} \sum_{k\in\text{anomal}} f_{0,A}\exp(-i\mathbf{G}\cdot\tau_k) \tag{69}$$

$$= S^0_{\mathbf{G}} + \frac{f'_A(E)+if''_A(E)}{f_{0,A}} S^A_{\mathbf{G}} \tag{70}$$

$$S^0_{\mathbf{G}} = |S^0_{\mathbf{G}}|\exp[i\phi^0(\mathbf{G})], \quad S^A_{\mathbf{G}} = |S^A_{\mathbf{G}}|\exp[i\phi^A(\mathbf{G})] \tag{71}$$

$$\begin{aligned} I &= S^*_{\mathbf{G}} S_{\mathbf{G}} = \left\{|S^0_{\mathbf{G}}|\exp[-i\phi^0(\mathbf{G})] + \frac{f'_A(E)-if''_A(E)}{f_{0,A}}|S^A_{\mathbf{G}}|\exp[-i\phi^A(\mathbf{G})]\right\}\times \\ &\quad \left\{|S^0_{\mathbf{G}}|\exp[i\phi^0(\mathbf{G})] + \frac{f'_A(E)+if''_A(E)}{f_{0,A}}|S^A_{\mathbf{G}}|\exp[i\phi^A(\mathbf{G})]\right\} \end{aligned} \tag{72}$$

$$\begin{aligned} &= |S^0_{\mathbf{G}}|^2 + \frac{(f'_A(E))^2+(f''_A(E))^2}{f^2_{0,A}}|S^A_{\mathbf{G}}|^2 + \frac{f'_A(E)+if''_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\exp[-i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))] \\ &\quad + \frac{f'_A(E)-if''_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\exp[i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))] \\ &= |S^0_{\mathbf{G}}|^2 + \frac{(f'_A(E))^2+(f''_A(E))^2}{f^2_{0,A}}|S^A_{\mathbf{G}}|^2 \\ &\quad + \frac{f'_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\left\{\exp[-i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))] + \exp[i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))]\right\} \\ &\quad + i\frac{f''_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\left\{\exp[-i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))] - \exp[i(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))]\right\} \\ &= |S^0_{\mathbf{G}}|^2 + \frac{(f'_A(E))^2+(f''_A(E))^2}{f^2_{0,A}}|S^A_{\mathbf{G}}|^2 + 2\frac{f'_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\cos(\phi^0(\mathbf{G})-\phi^A(\mathbf{G})) \\ &\quad + 2\frac{f''_A(E)}{f_{0,A}}|S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\sin(\phi^0(\mathbf{G})-\phi^A(\mathbf{G})) \end{aligned} \tag{73}$$

吸収端のエネルギー前後で $f'_A(E), f''_A(E)$ を実験的に求める。（タンパクの解析では S を置換した Se が異常分散を示す原子として使用されることが多い。。）吸収端前後の 3 つまたは 4 つの波長の X 線を用いて，X 線散乱強度をもとめる。$|S^0_{\mathbf{G}}|^2, |S^A_{\mathbf{G}}|^2, |S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\cos(\phi^0(\mathbf{G})-\phi^A(\mathbf{G})), |S^0_{\mathbf{G}}||S^A_{\mathbf{G}}|\sin(\phi^0(\mathbf{G})-\phi^A(\mathbf{G}))$ が決定される。$|S^A_{\mathbf{G}}|^2$ をフーリエ変換したもの (Patterson 関数) から，異常分散を示す原子の位置を推定する。異常分散を示す原子の位置がわかれば，$\phi^A(\mathbf{G})$ が決定でき，さらに $\phi^0(\mathbf{G})$ が上の関係から決定できるので，最終的に原子の構造が確定する。

詳細は，http://skuld.bmsc.washington.edu/scatter/AS_ index.html X-ray Anomalous Scattering by Ethan A Merritt c1996-2006 を参照のこと。

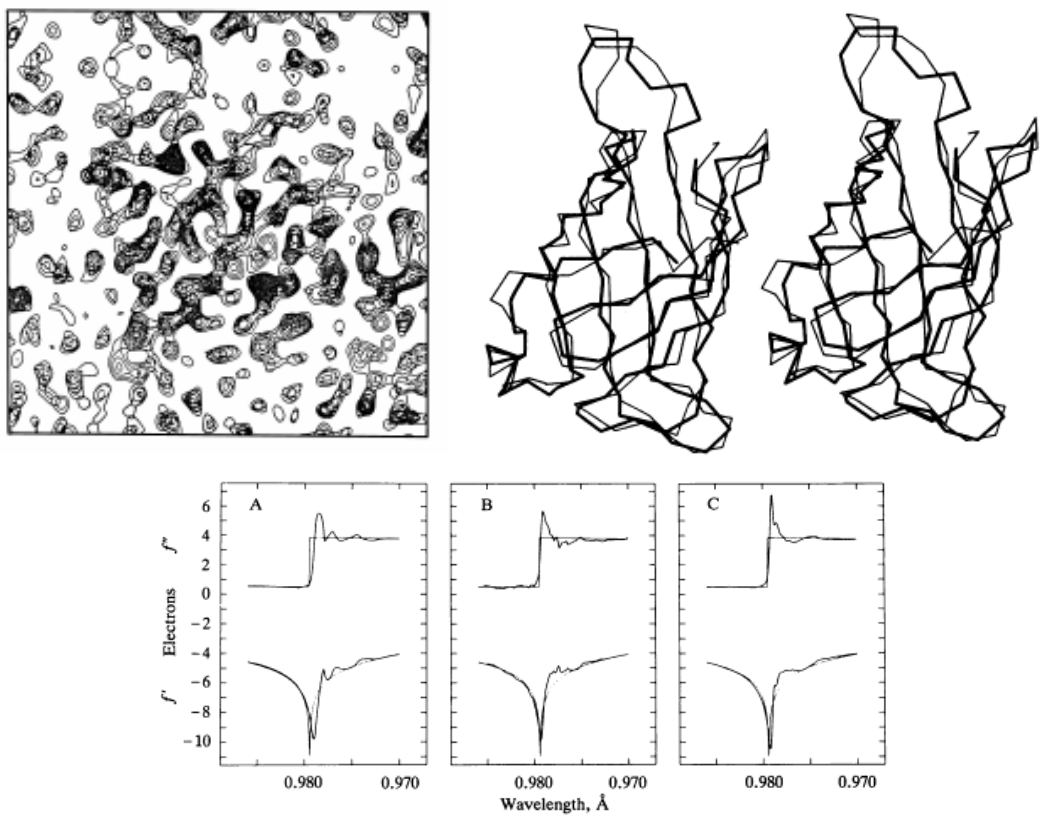


Figure 4: 多波長異常分散法による selenobiotinyl streptavidin の 3.3Åでの異常分散効果のみによる電子密度図, selenobiotinyl streptavidin の構造，Se の異常分散の異方性（A:**E**(電場ベクトル)//**a**(結晶の **a** 軸), B:**E**//**b**, C:**E**//**c** Proc Natl Acad Sci U S A. 1989, 86, 2190–2194. Crystal structure of core streptavidin determined from multiwavelength anomalous diffraction of synchrotron radiation. W A Hendrickson, A Pahler, J L Smith, Y Satow, E A Merritt, and R P Phizackerley