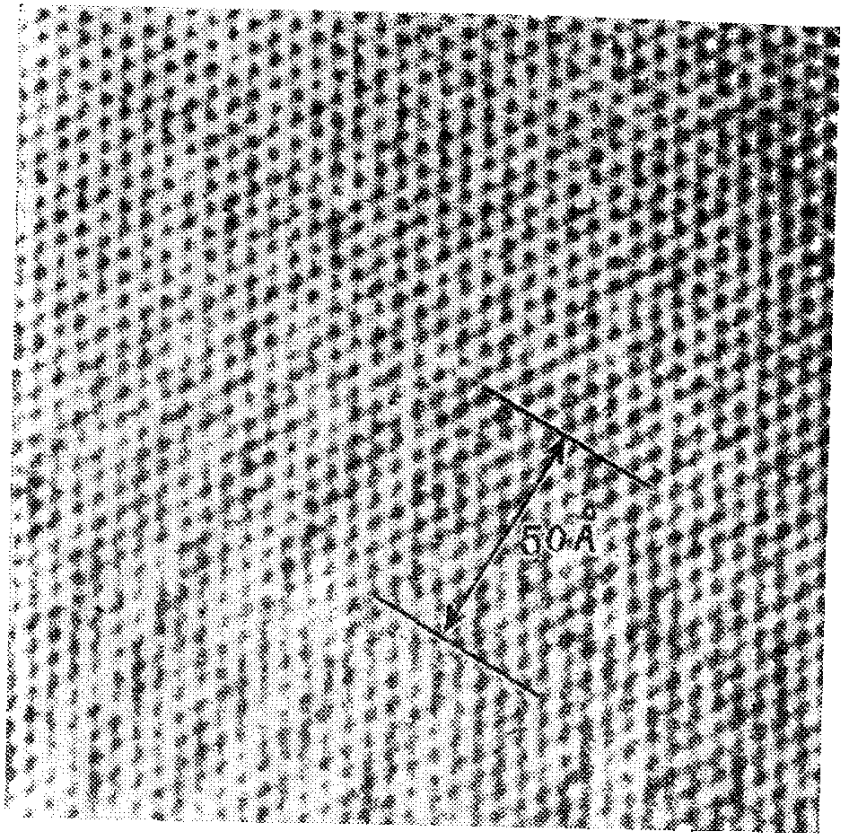
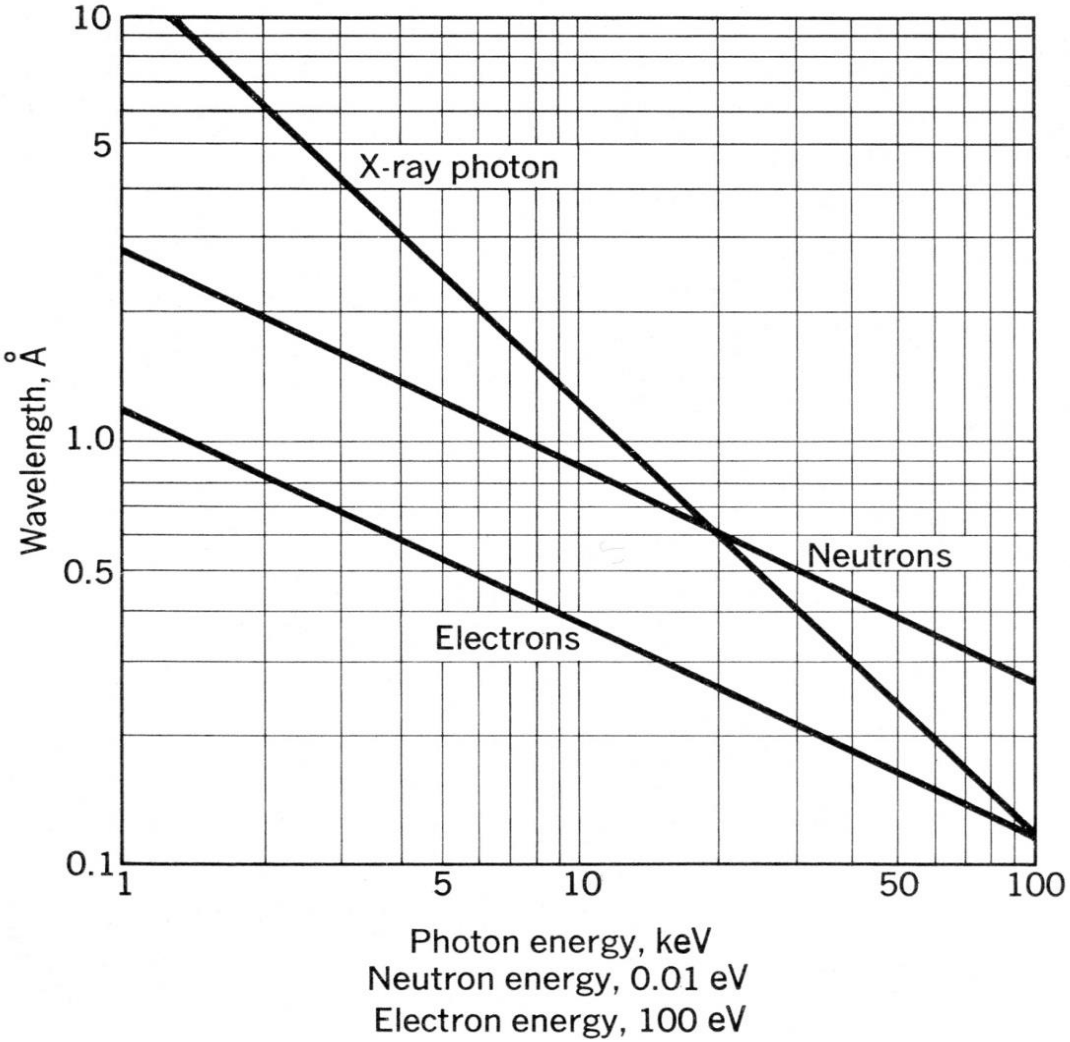
Experimental studies of crystal structure



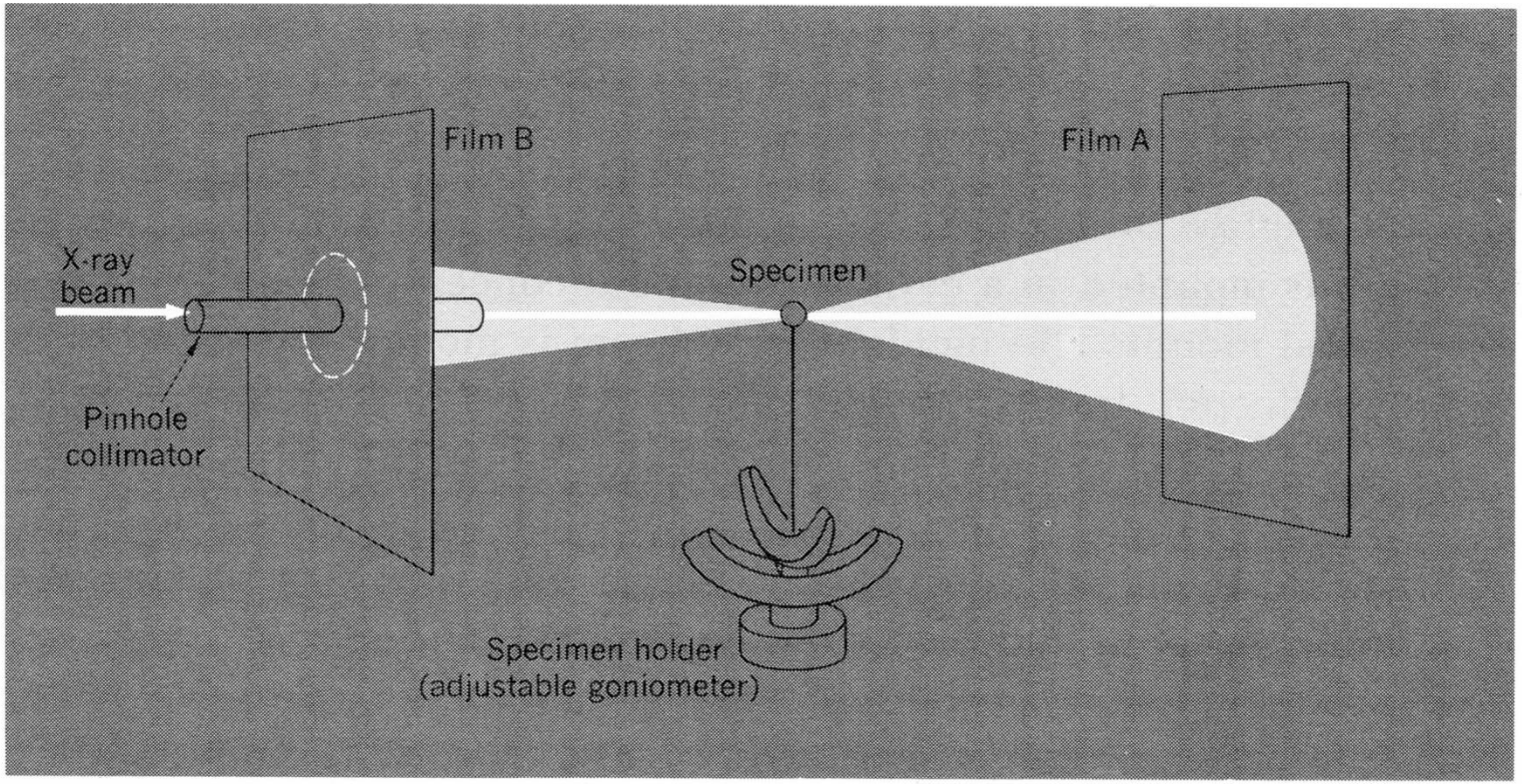
Electron-microscope photograph of atomic planes of a crystal $Al_2O_3 \cdot 4SiO_2$-H_2O.
An increase 3 250 000 times.

x-ray, electron and neutron diffraction



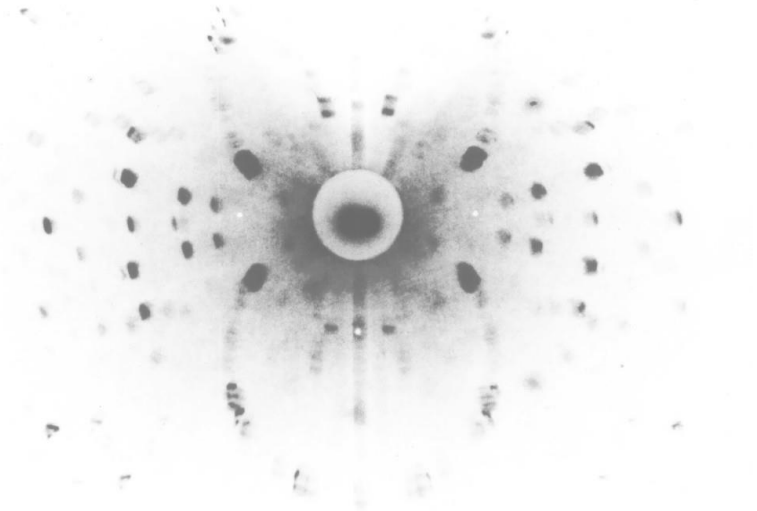
3 types of x-ray diffraction (1).

(1) A Laue camera. With a non-monochromatic x-ray beam, the camera produces Laue patterns useful, e.g., for the orientation of single crystals. Angle is fixed.

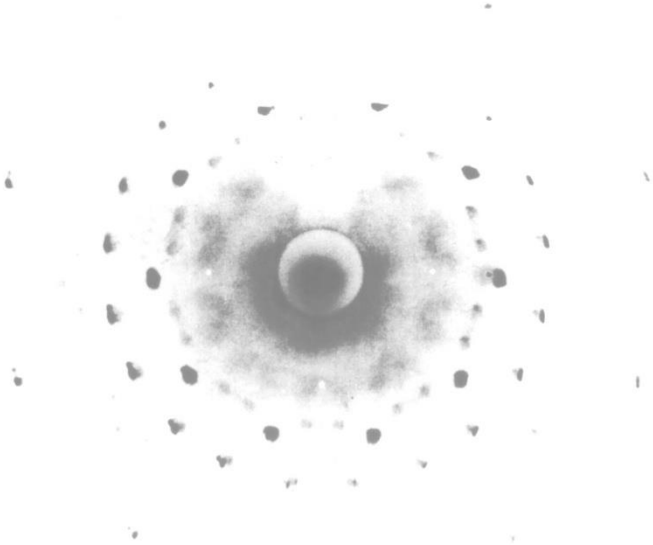


[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

Example: the Laue pattern obtained from a single crystal of the decagonal Al-Ni-Co phase (S1 type superstructure)



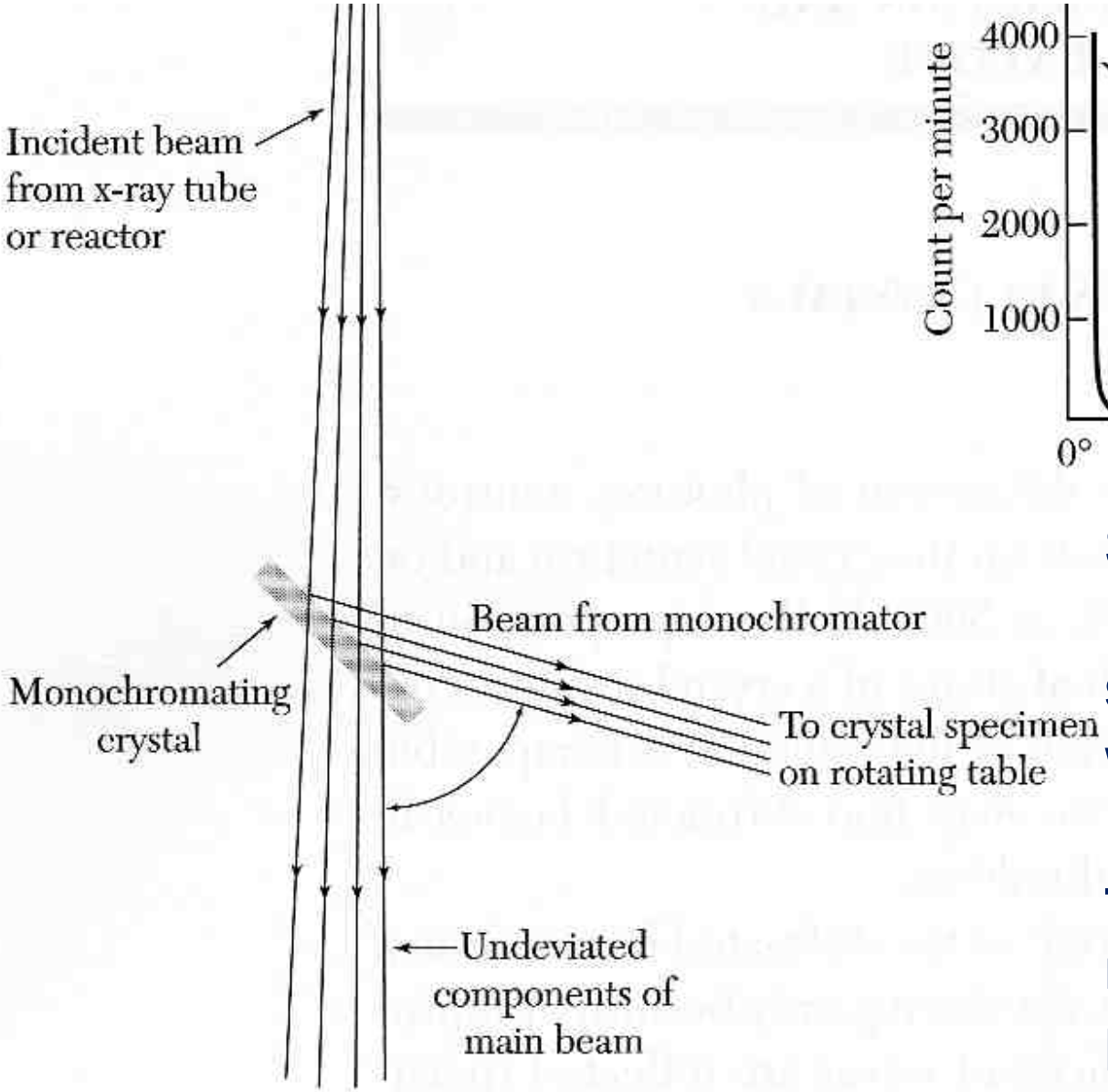
incident beam along the A_2 axis

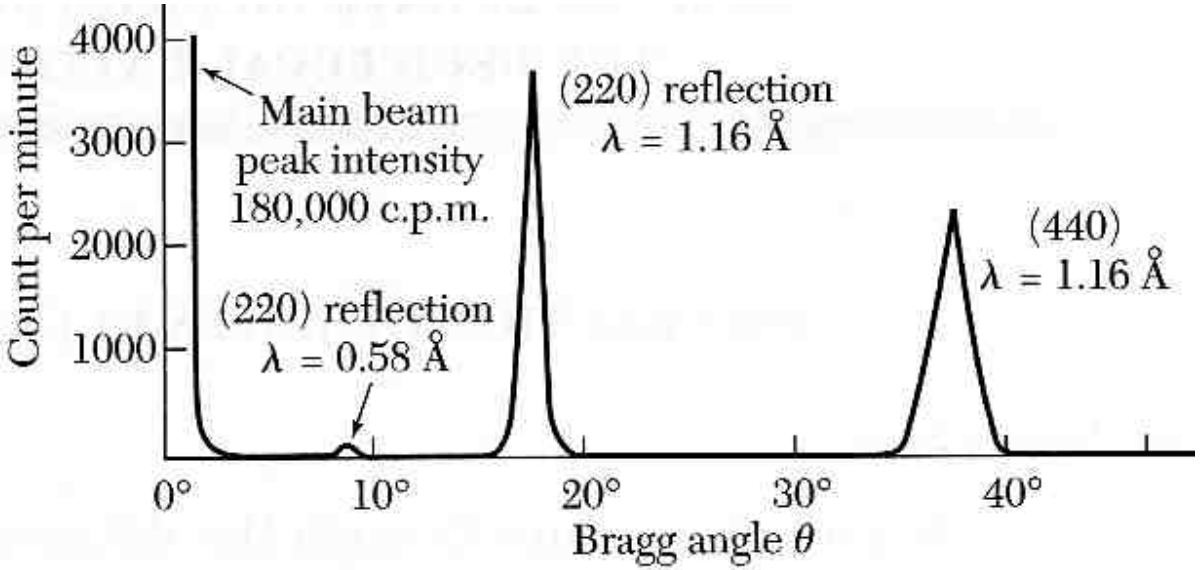


incident beam along the A_{10} axis

This method mainly gives the symmetry axes of the crystal

3 types of x-ray diffraction. (2) rotating crystal in monochromatic beam





Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 A beam of neutrons from a calcium fluoride crystal monochromator. The main beam is that not reflected from the second crystal.

3 types of x-ray diffraction. (3) powder method.

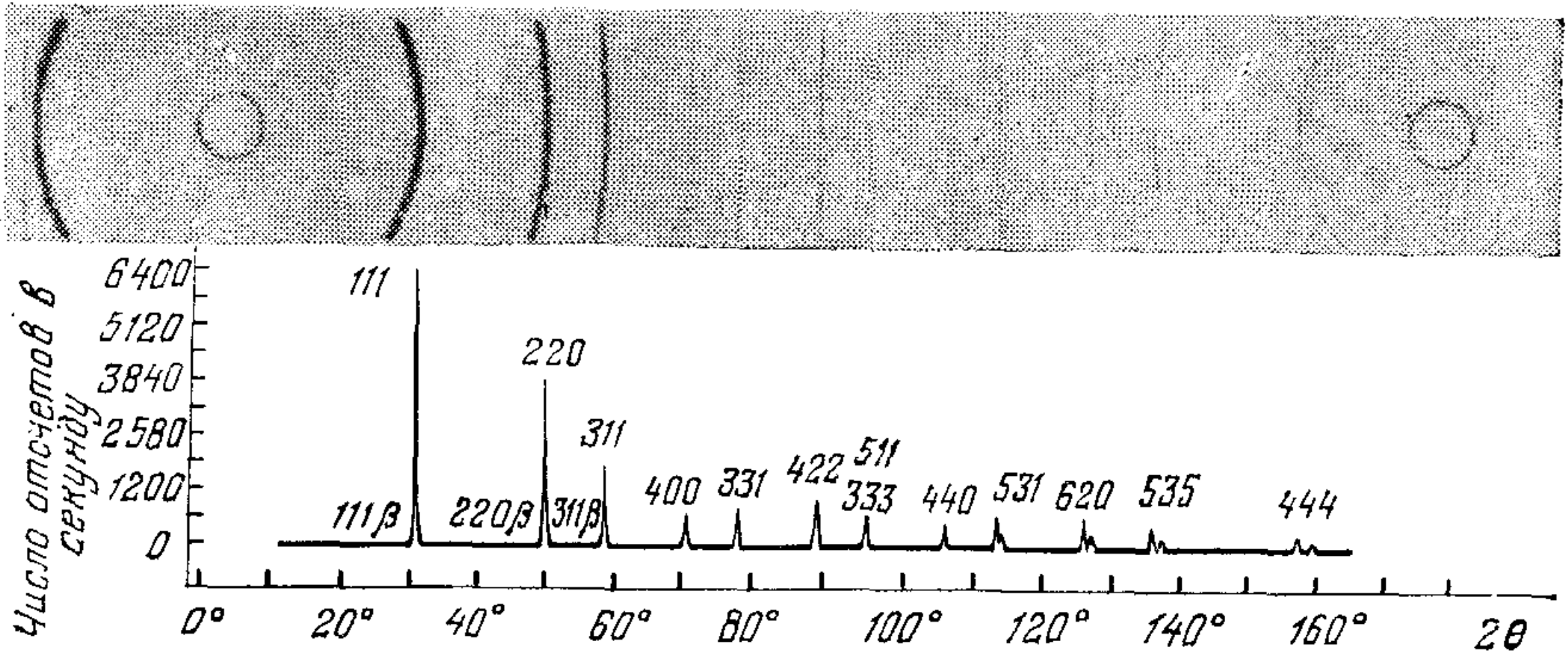
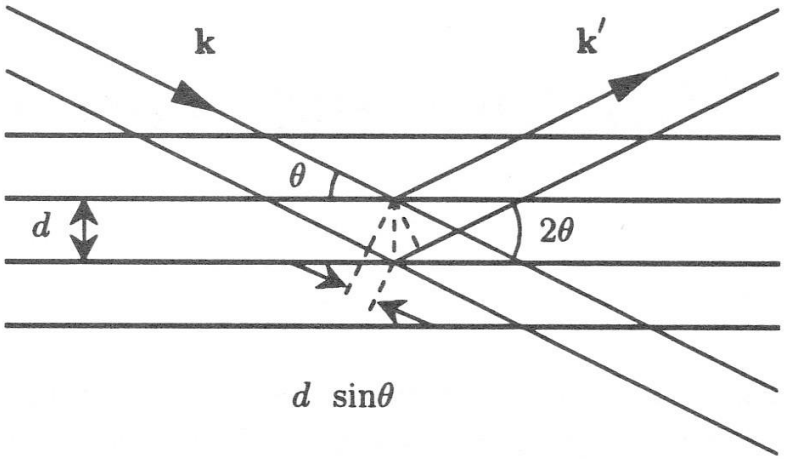


Рис. 2.13. Рентгенограммы кремния, полученные методом порошка (верхняя) и с помощью рентгеновского дифрактометра (нижняя). Верхняя рентгенограмма получена путем регистрации отраженных лучей на пленку, нижняя — с помощью счетчика отраженных лучей. (W. Parrish.)

Do not need mono-crystal samples

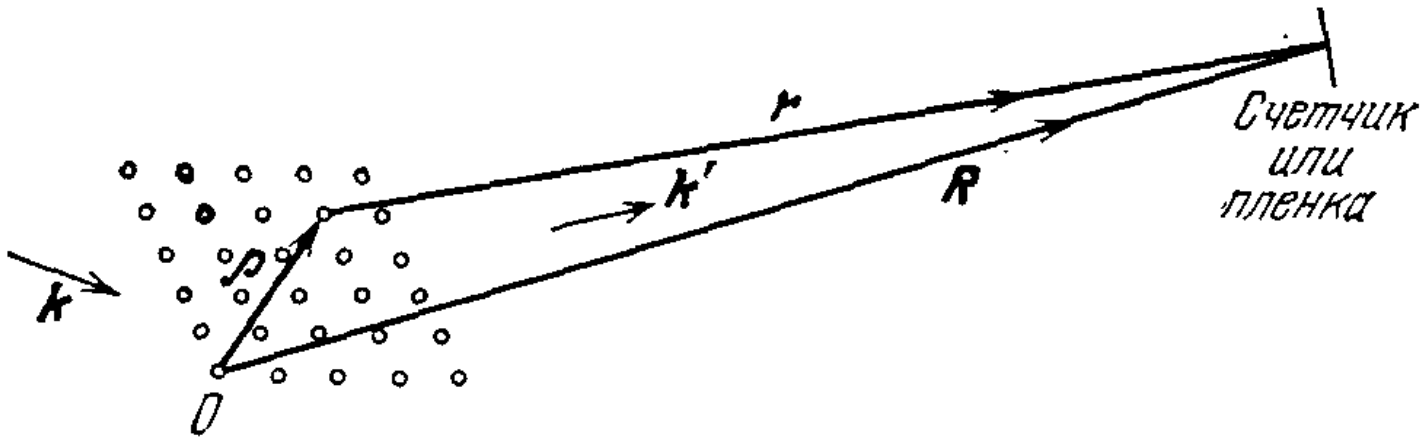
Scattering from parallel planes showing the origin of Bragg's law. The planes are separated by a distance *d*.

The incident wave vector is **k** and the scattered wave vector is **k**'. The magnitude of both **k** and **k**' is $2\pi/\lambda$, and the path difference between waves partially reflected from successive planes is $2d\sin\theta$.



[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

Derivation of diffraction condition



$$r = R\left[1 - \frac{2\rho}{R}\cos(\boldsymbol{\rho}, \boldsymbol{R}) + \left(\frac{\rho}{R}\right)^2\right]^{1/2} \approx R\left(1 - \frac{\rho}{R}\cos(\boldsymbol{\rho}, \boldsymbol{R}) + \ldots\right)$$

$$e^{i(\boldsymbol{k}\cdot\boldsymbol{\rho}+kr)} = e^{ikR}\exp\{i[\boldsymbol{k}\cdot\boldsymbol{\rho} - k\rho\cos(\boldsymbol{\rho}, \boldsymbol{R})]\}$$

$$k\rho\cos(\boldsymbol{\rho}, \boldsymbol{R}) = k'\rho\cos(\boldsymbol{\rho}, \boldsymbol{k}') = \boldsymbol{k}'\cdot\boldsymbol{\rho}.$$

$$e^{i(\boldsymbol{k}\cdot\boldsymbol{\rho}+kr)} = e^{ikR}\exp[i(\boldsymbol{k}\cdot\boldsymbol{\rho} - \boldsymbol{k}'\cdot\boldsymbol{\rho})] = e^{ikR}\exp(-i\boldsymbol{\rho}\cdot\Delta\boldsymbol{k}),$$

$$E_{sc}(r) = \left(\frac{CE_0\, e^{ikR}\, e^{-i\omega t}}{R}\right)\exp(-i\boldsymbol{\rho}_{mnp}\cdot\Delta\boldsymbol{k}),$$

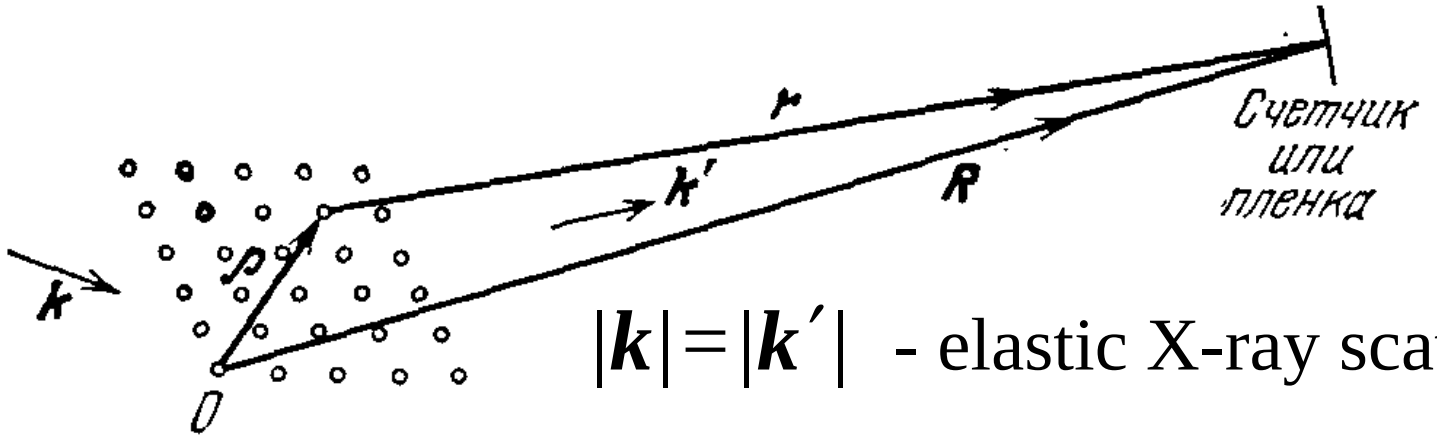
Amplitude of diffracted wave

$$\mathcal{A} = \sum_{mnp}\exp(-i\boldsymbol{\rho}_{mnp}\cdot\Delta\boldsymbol{k}).$$

For point scattering centers:

$$\boldsymbol{\rho}_{mnp} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c},$$

Derivation of diffraction condition



$|\boldsymbol{k}|=|\boldsymbol{k}'|$ - elastic X-ray scattering; $\boldsymbol{r} = \boldsymbol{R}-\boldsymbol{\rho}$ =>

$$\phi_0=exp(i\boldsymbol{k}'\boldsymbol{R})$$

$$\phi_\rho=exp(i\boldsymbol{k}\boldsymbol{\rho}+i\boldsymbol{k}'\boldsymbol{r})= exp(i\boldsymbol{k}'\boldsymbol{R})\ exp\ (i\boldsymbol{k}\boldsymbol{\rho}-i\boldsymbol{k}'\boldsymbol{\rho})]= \phi_0\, exp(-i\boldsymbol{\Delta k}\boldsymbol{\rho})$$

Amplitude of diffracted wave $\mathscr{A} \equiv \sum_{mnp} \exp\,(-\,i\mathfrak{o}_{mnp}\cdot\Delta\boldsymbol{k}).$

For point scattering centers:

$$\mathfrak{o}_{mnp} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c},$$

Derivation of diffraction condition (result) for simple point lattice

For point scattering centers the scattering amplitude is maximal ($\mathscr{A}_{\max} = M^3$) if

$$\mathscr{A} = \sum_{mnp} \exp\left[-i\left(m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}\right)\cdot\Delta\boldsymbol{k}\right].$$

$$\rho_{mnp}\cdot\Delta\boldsymbol{k} = \left(m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}\right)\cdot\Delta\boldsymbol{k} = 2\pi\cdot(\text{целое число})$$

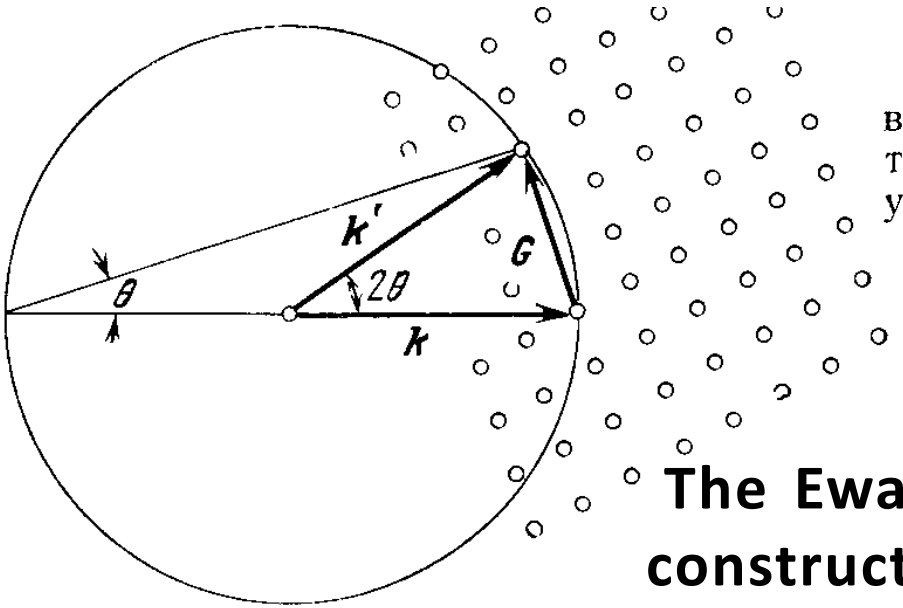
The diffraction condition:

$$\boldsymbol{a}\cdot\Delta\boldsymbol{k} = 2\pi h, \quad \boldsymbol{b}\cdot\Delta\boldsymbol{k} = 2\pi k, \quad \boldsymbol{c}\cdot\Delta\boldsymbol{k} = 2\pi l$$

is satisfied for any vector of reciprocal lattice $\boldsymbol{G} = h\boldsymbol{A} + k\boldsymbol{B} + l\boldsymbol{C}$

where

$$\boldsymbol{A} = 2\pi\frac{\boldsymbol{b}\times\boldsymbol{c}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}}, \quad \boldsymbol{B} = 2\pi\frac{\boldsymbol{c}\times\boldsymbol{a}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}}, \quad \boldsymbol{C} = 2\pi\frac{\boldsymbol{a}\times\boldsymbol{b}}{\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}}$$



The Ewald construction

Построение Эвальда. Имеются два условия дифракции: первое — условие для частоты, второе — условие для волнового вектора. Объединение этих двух условий приводит к наиболее удачному геометрическому выражению условия дифракции.

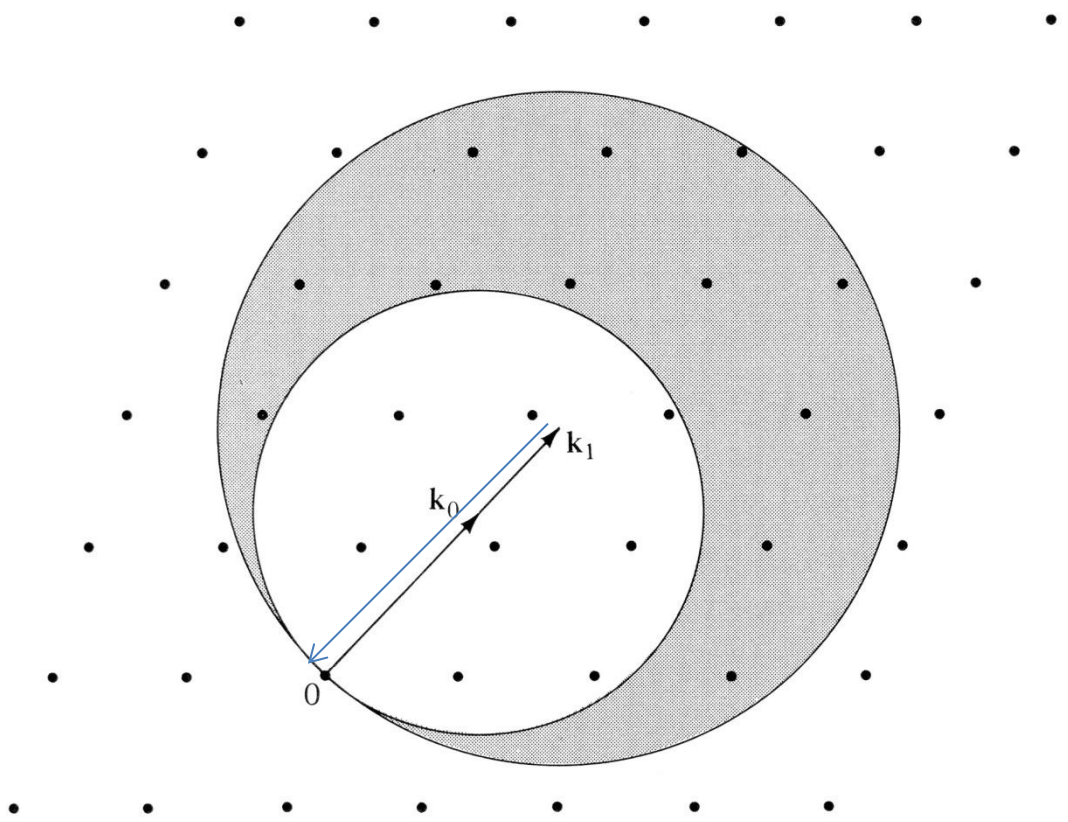
$$\hbar\omega' = \hbar\omega \Rightarrow k' = k$$

$$\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G} \Rightarrow 2\boldsymbol{k}\cdot\boldsymbol{G} + G^2 = 0$$

(h,k,l) denote the reflection peak

The Ewald construction for the Laue method. The incident X-ray beam is non-monochromatic, i.e., $\mathbf{k}_0 \leq \mathbf{k} \leq \mathbf{k}_1$. The Ewald spheres for all incident $\mathbf{k}$ fill the shaded region between the spheres centered on the tips of the vectors $\mathbf{k}_0$ and $\mathbf{k}_1$, respectively.

The Laue classes.



[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

Structure factor of the basis

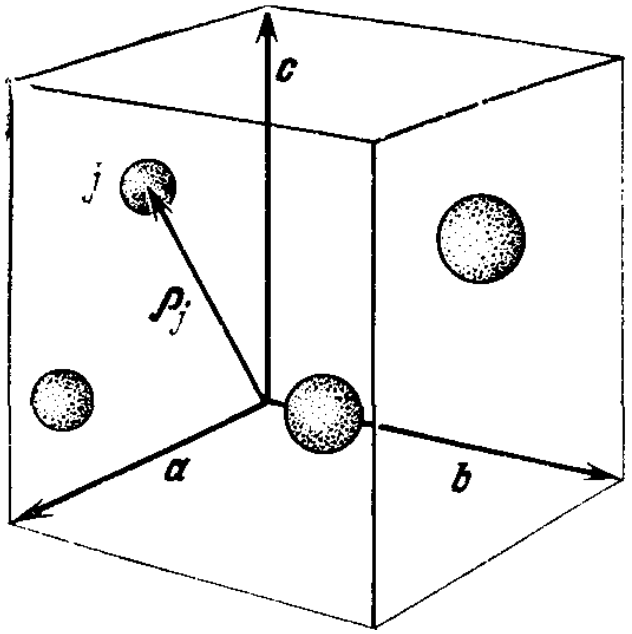


Рис. 2.29. Положение j-го атома в элементарной ячейке задано вектором $\varrho_j = x_j\boldsymbol{a} + y_j\boldsymbol{b} + z_j\boldsymbol{c}$, где x_j, y_j, z_j — константы

Electron concentration from each atom is given by $c_j(\varrho - \varrho_j - \varrho_{mnp})$

where $\varrho_{mnp} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$

and $\varrho_j = x_j\boldsymbol{a} + y_j\boldsymbol{b} + z_j\boldsymbol{c},$

The total electron concentration is

$$n(\varrho) = \sum_{mnp} \sum_{j=1}^{s} c_j(\varrho - \varrho_j - \varrho_{mnp})$$

$$\mathscr{A}_{\Delta k} = \int dV\, n(\varrho) \exp(-i\varrho \cdot \Delta\boldsymbol{k}) =$$

$$= \left(\sum_{mnp} \exp(-i\varrho_{mnp} \cdot \Delta\boldsymbol{k})\right)\left(\sum_j f_j \exp(-i\varrho_j \cdot \Delta\boldsymbol{k})\right)$$

where the atomic form factor $f_j = \int dV\, c_j(\varrho') \exp(-i\varrho' \cdot \Delta\boldsymbol{k}),$

The sum $\mathscr{S}_{\boldsymbol{G}} = \sum_j f_j \exp(-i\varrho_j \cdot \boldsymbol{G})$ **is called structural factor of the basis**

$$\mathscr{S}(hkl) = \sum_j f_j \exp[-i2\pi(x_j h + y_j k + z_j l)]$$

It gives the relative amplitudes of different Bragg reflection peaks.

Структурный фактор ОЦК решетки. Базис ОЦК решетки состоит из двух одинаковых атомов. Их координаты в обычной элементарной кубической ячейке равны 000 и $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, т. е. для одного из атомов $x_1 = y_1 = z_1 = 0$, а для другого $x_2 = y_2 = z_2 = {}^1/_2$. Тогда (2.61) принимает вид

$$\mathscr{S}(hkl) = f\{1 + \exp[-i\pi(h + k + l)]\}, \qquad (2.62)$$

где f — рассеивающая способность отдельного атома. Величина $\mathscr{S}$ равна нулю в тех случаях, когда значение экспоненты равно -1, т. е. во всех тех случаях, когда ее показатель есть нечетное число, помноженное на $-i\pi$. Тогда имеем:

$\mathscr{S} = 0$, если сумма $h + k + l$ равна нечетному целому числу;

$\mathscr{S} = 2f$, если эта сумма равна четному целому числу.

В дифракционной картине металлического натрия, имеющего ОЦК решетку, отсутствуют отражения, обусловленные плоскостями (100), (300), (111), (221), однако отражения, определяемые плоскостями (200), (110) и (222), будут присутствовать; указанные индексы плоскостей (hkl) соответствуют кубической ячейке.

Explanation of the absence of a (100) reflection from a body-centered cubic lattice.

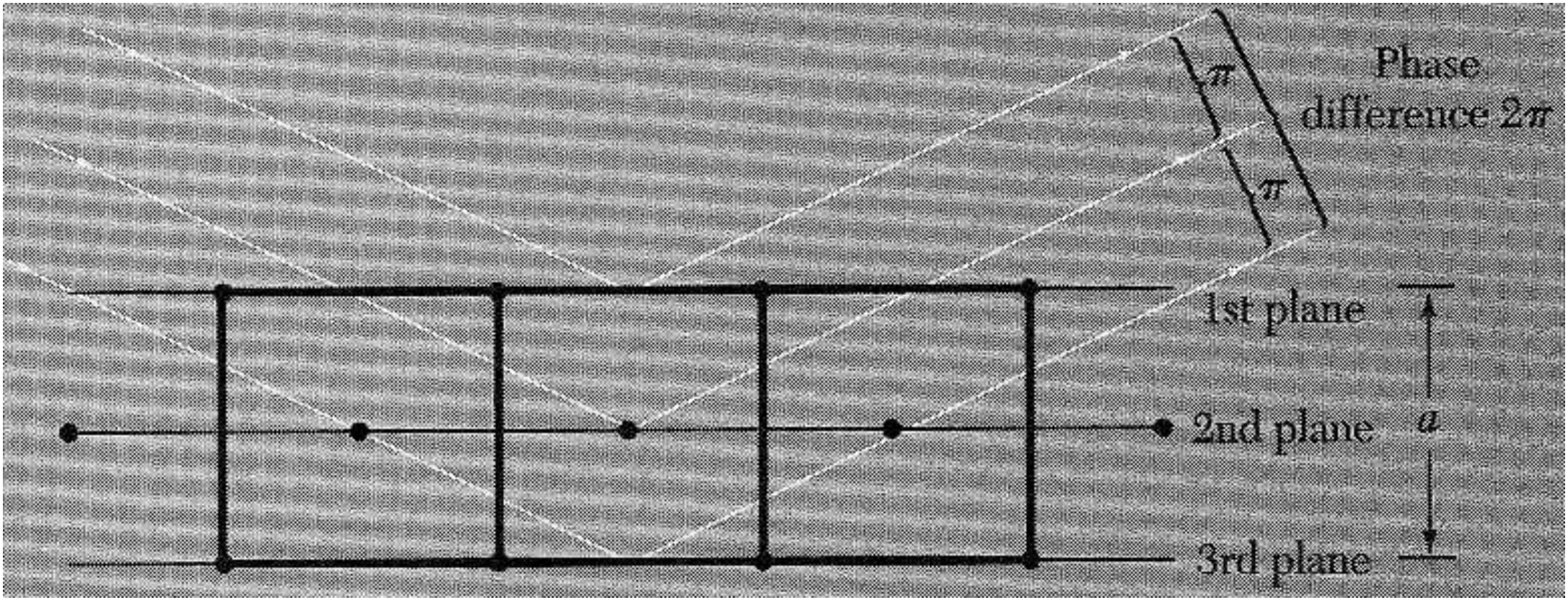


Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π, so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

Structure Factor of the fcc Lattice

The basis of the fcc structure referred to the cubic cell has identical atoms at 000; $0\frac{11}{22}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{11}{22}0$. Thus (46) becomes

$$S(v_1v_2v_3) = f\{1 + \exp[-i\pi(v_2 + v_3)] + \exp[-i\pi(v_1 + v_3)] + \exp[-i\pi(v_1 + v_2)]\} . \tag{48}$$

If all indices are even integers, $S = 4f$; similarly if all indices are odd integers. But if only one of the integers is even, two of the exponents will be odd multiples of $-i\pi$ and S will vanish. If only one of the integers is odd, the same argument applies and S will also vanish.

Thus in the fcc lattice no reflections can occur for which the indices are partly even and partly odd. The point is beautifully illustrated by Fig. 17: both KCl and KBr have an fcc lattice, but KCl simulates an sc lattice because the K^+ and Cl^- ions have equal numbers of electrons.

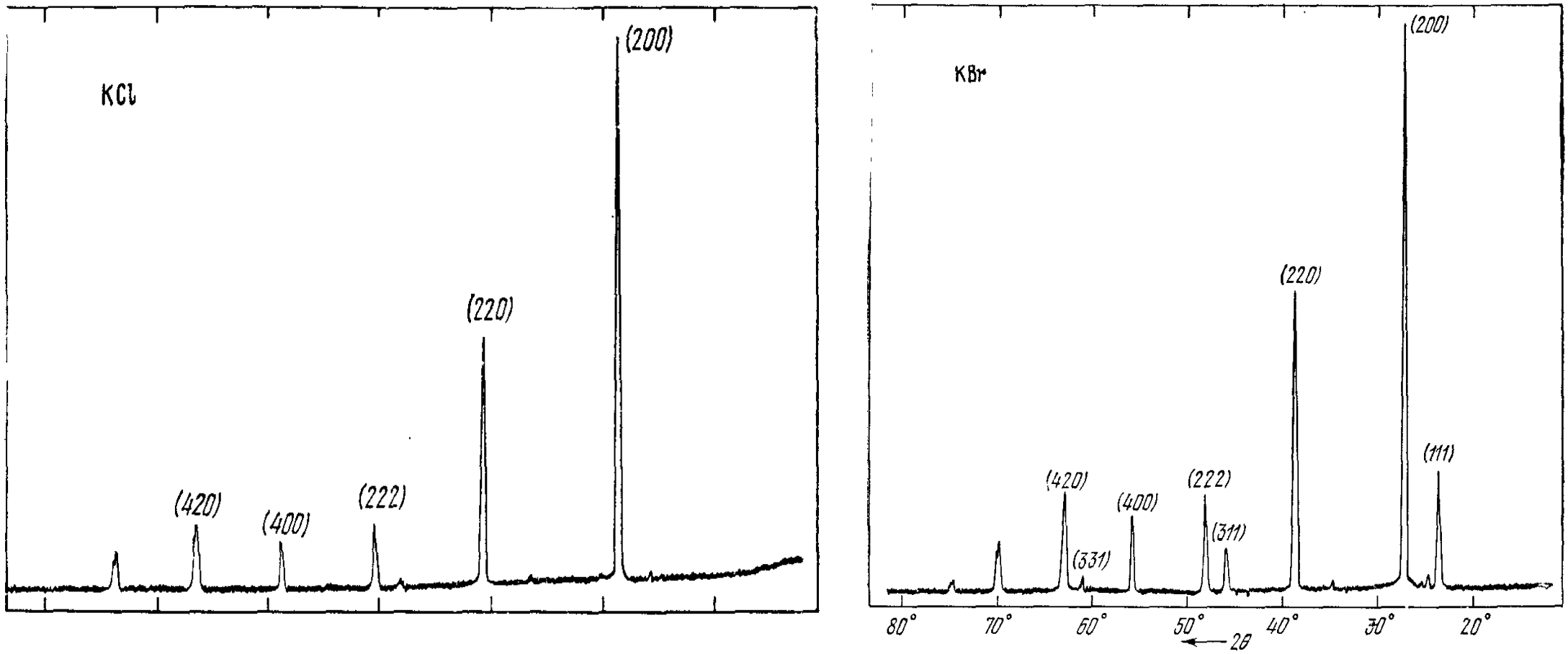


Fig. 17. Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant a/2. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a. In KBr the form factor of Br^- is quite different than that of K^+, and all reflections of the free lattice are present.

Atomic form-factor $f_G = \int dV\, c(r)\, e^{-ir\cdot G}$

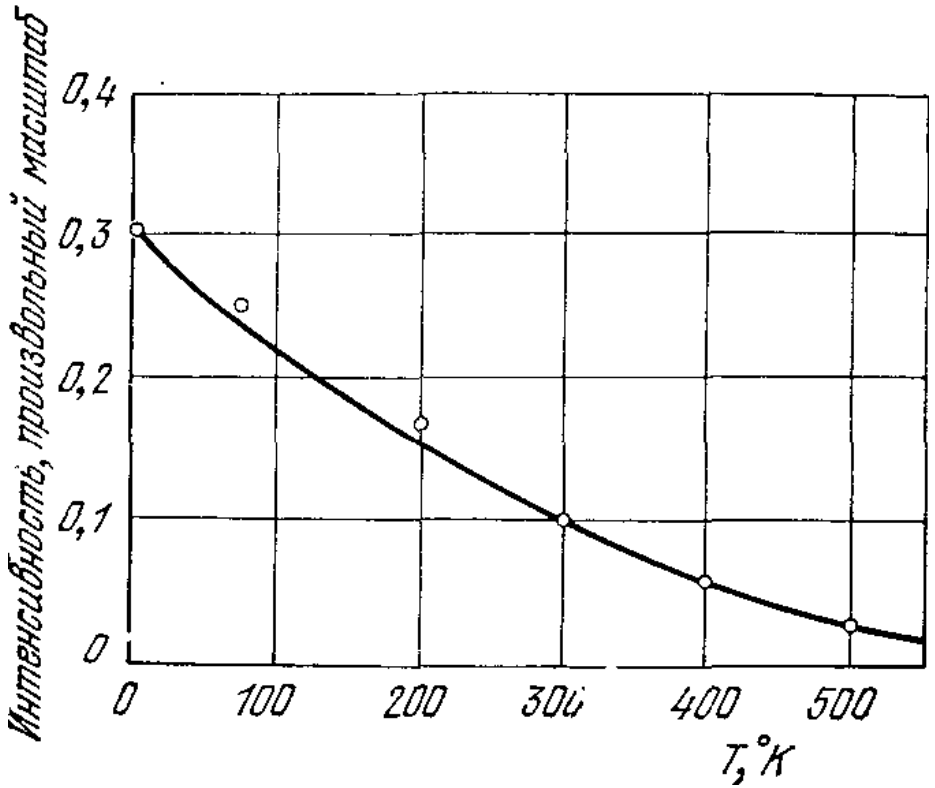
For spherically symmetric electron distribution in atom $f_G = 4\pi \int dr\, c(r)\, r^2 \frac{\sin Gr}{Gr}$

$$f_G \equiv 2\pi \int r^2\, dr\, d(\cos\alpha)\, c(r)\, e^{-iGr\cos\alpha} = 2\pi \int dr\, r^2 c(r) \frac{e^{iGr} - e^{-iGr}}{iGr}$$

If the electron density was located $(\sin Gr)/Gr = 1$ and for all *G* only in the center of the atom, then $f_G = 4\pi \int dr\, c(r)\, r^2 = Z$

where Z is the number of atomic electrons. Therefore f_G is the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by one electron localized at a point.

Temperature dependence of reflection line intensity



Instant atom position is $\rho(t) = \rho_0 + u(t),$

The average scattering amplitude is

$$\langle \mathcal{A} \rangle = \mathcal{A}_0 \langle \exp(-iu \cdot G) \rangle,$$

$$\langle \exp(-iu \cdot G) \rangle = 1 - i\langle u \cdot G \rangle - \frac{1}{2}\langle (u \cdot G)^2 \rangle +$$

using the averages

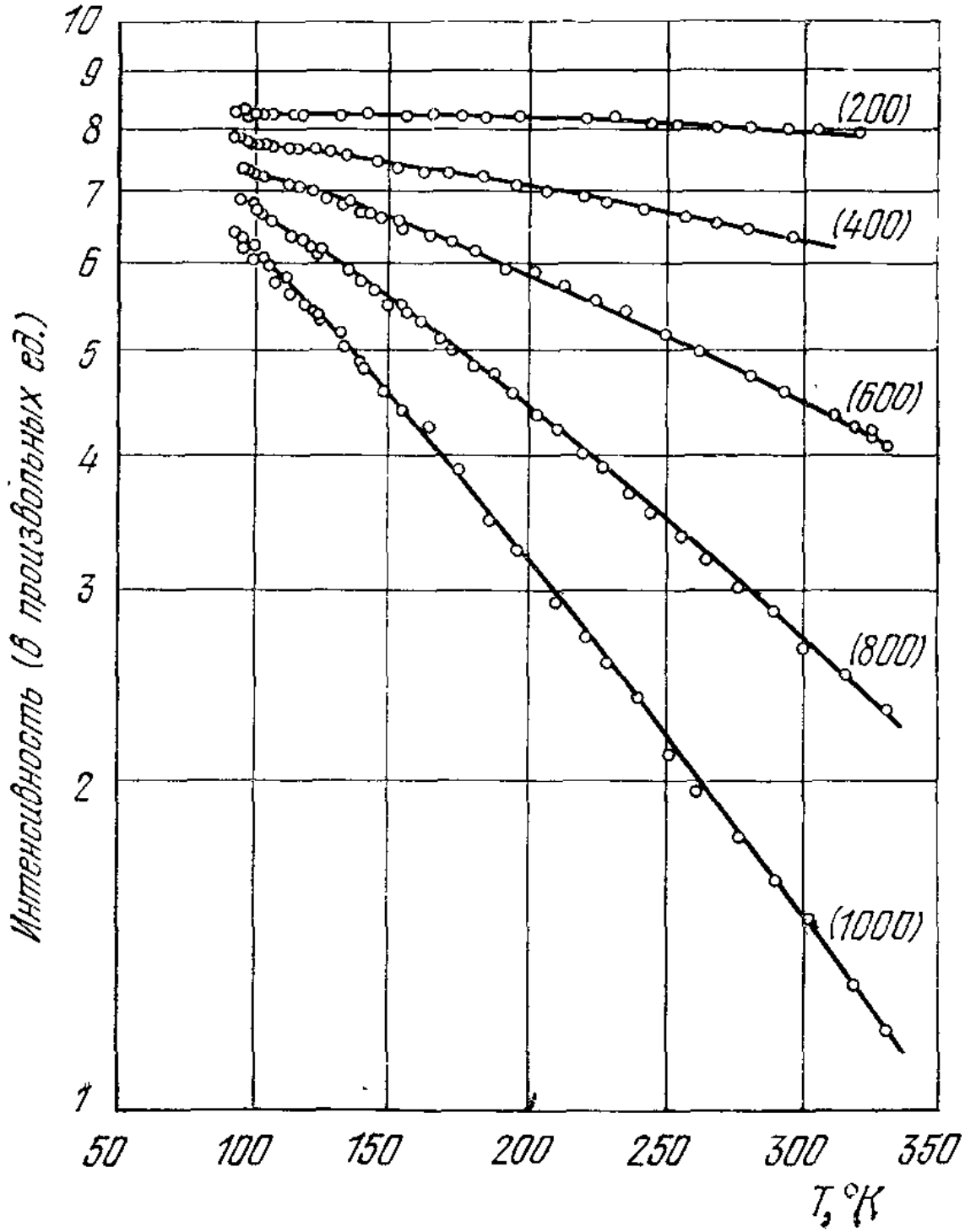
$$\langle u \cdot G \rangle = 0 \quad \langle (u \cdot G)^2 \rangle = \frac{1}{3}\langle u^2 \rangle G^2.$$

and the expansion $\exp\left[-\frac{1}{6}\langle u^2 \rangle G^2\right] = 1 - \frac{1}{6}\langle u^2 \rangle G^2 + \ldots$

we obtain the intensity the Debye-Waller factor of temperature damping:

$$I = I_0 \exp\left[-\frac{1}{3}\langle u^2 \rangle G^2\right],$$

where I_0 is the intensity without atom motion.



Temperature dependence of the diffraction maximum intensity (h00) for aluminum. Reflections (h00) with odd h values are forbidden in the fcc structure.

The reciprocal lattice

Consider a set of points $\mathbf{R}$ constituting a Bravais lattice, and a plane wave, $e^{i\mathbf{kr}}$.

The set of all wave vectors $\mathbf{K}$ that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.

A reciprocal lattice is defined with reference to a particular Bravais lattice.

The Bravais lattice that determines a given reciprocal lattice is often referred to as the direct lattice, when viewed in relation to its reciprocal.

Reciprocal lattice

The reciprocal lattice is itself a Bravais lattice but in momentum space

Let $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ be a set of primitive vectors for the direct lattice.

Then the three primitive vectors

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

can generate the reciprocal lattice.

The reciprocal of the reciprocal lattice is the original direct lattice.

ЗОНЫ БРИЛЛЮЭНА

Зона Бриллюэна представляет собой ячейку Вигнера — Зейтца в обратной решетке. (Ячейка Вигнера — Зейтца прямой решетки показана на рис. 1.8.) Определенная таким образом зона Бриллюэна является наглядной геометрической интерпретацией условия дифракции $2\boldsymbol{k}\cdot\boldsymbol{G}+G^2=0$. Сначала удобно в это условие подставить $-\boldsymbol{G}$ вместо $\boldsymbol{G}$, чтобы записать условие дифракции в форме

$$2\boldsymbol{k}\cdot\boldsymbol{G}=G^2. \tag{2.41}$$

Эта подстановка не меняет существо условия дифракции, поскольку, если $\boldsymbol{G}$ — вектор обратной решетки, то и $-\boldsymbol{G}$ также является вектором обратной решетки. Перепишем (2.41) следующим образом:

$$\boldsymbol{k}\cdot(^1/_2\boldsymbol{G})=(^1/_2\boldsymbol{G})^2. \tag{2.42}$$

Построим плоскость, перпендикулярную к вектору $\boldsymbol{G}$ и проходящую через его середину; тогда (рис. 2.21) *произвольный вектор* $\boldsymbol{k}$, *проведенный до этой плоскости из точки, выбранной за начало координат, будет удовлетворять условию дифракции.* Построенная таким образом плоскость образует часть границы зоны Бриллюэна.

Brillouin zones

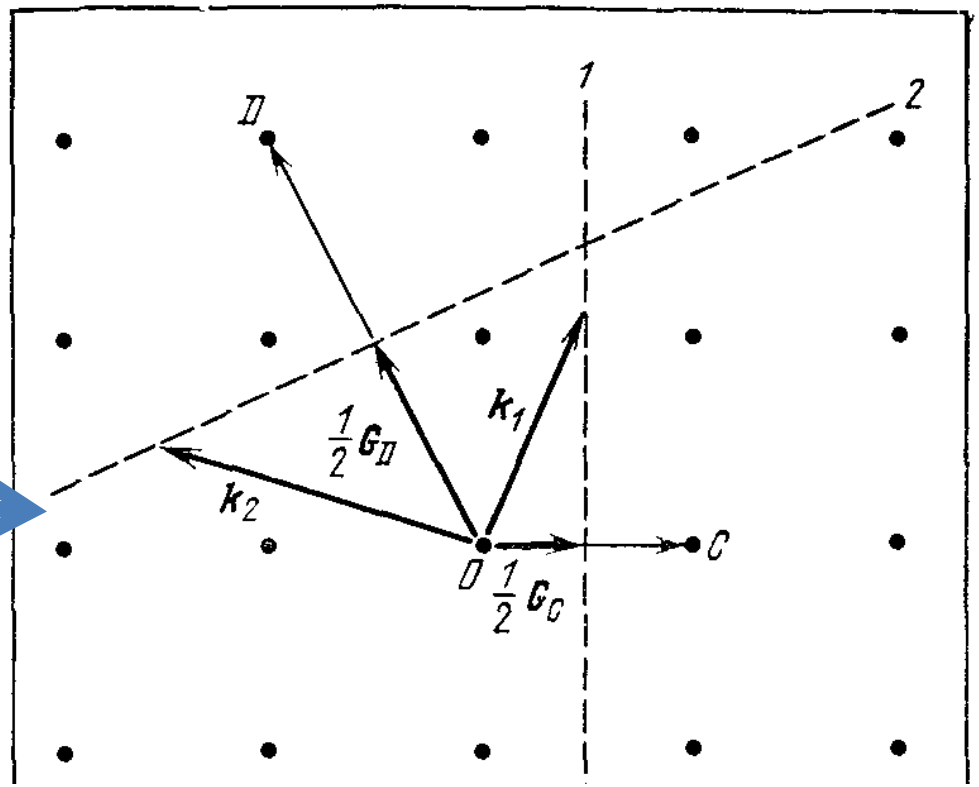
Brillouin gave the statement of the diffraction condition that is most widely used in solid state physics, which means in the description of electron energy band theory and of the elementary excitations of other kinds.
A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.

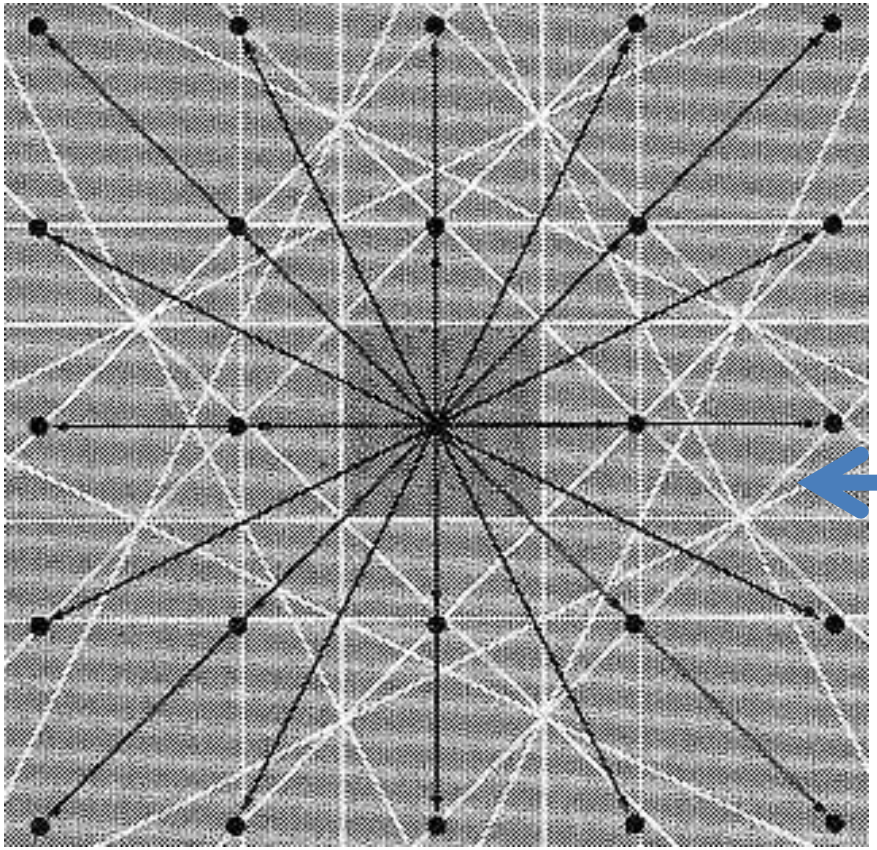
Brillouin zone gives a vivid geometrical interpretation of the diffraction condition $2\mathbf{k} \cdot \mathbf{G} = G^2$ of Eq. (23). We divide both sides by 4 to obtain

$$\mathbf{k} \cdot \left(\tfrac{1}{2}\mathbf{G}\right) = \left(\tfrac{1}{2}G\right)^2 \ . \qquad (26)$$

We now work in reciprocal space, the space of the $\mathbf{k}$'s and $\mathbf{G}$'s. Select a vector $\mathbf{G}$ from the origin to a reciprocal lattice point. Construct a plane normal to this vector $\mathbf{G}$ at its midpoint. This plane forms a part of a zone boundary (Fig. 9a). An x-ray beam in the crystal will be diffracted if its wavevector $\mathbf{k}$ has the magnitude and direction required by (26). The diffracted beam will then be in the direction $\mathbf{k} - \mathbf{G}$, as we see from (19) with $\Delta\mathbf{k} = -\mathbf{G}$. Thus the Brillouin construction exhibits all the wavevectors $\mathbf{k}$ which can be Bragg-reflected by the crystal.

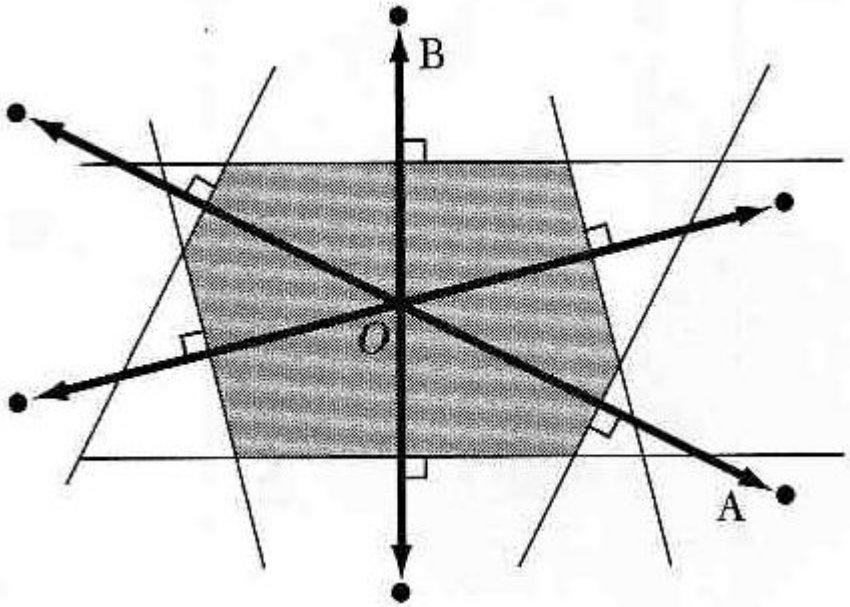
Figure 9a Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD. Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively. Any vector from the origin to the plane 1, such as $\mathbf{k}_1$, will satisfy the diffraction condition $\mathbf{k}_1 \cdot (\frac{1}{2}\mathbf{G}_C) = (\frac{1}{2}\mathbf{G}_C)^2$. Any vector from the origin to the plane 2, such as $\mathbf{k}_2$, will satisfy the diffraction condition $\mathbf{k}_2 \cdot (\frac{1}{2}\mathbf{G}_D) = (\frac{1}{2}\mathbf{G}_D)^2$.



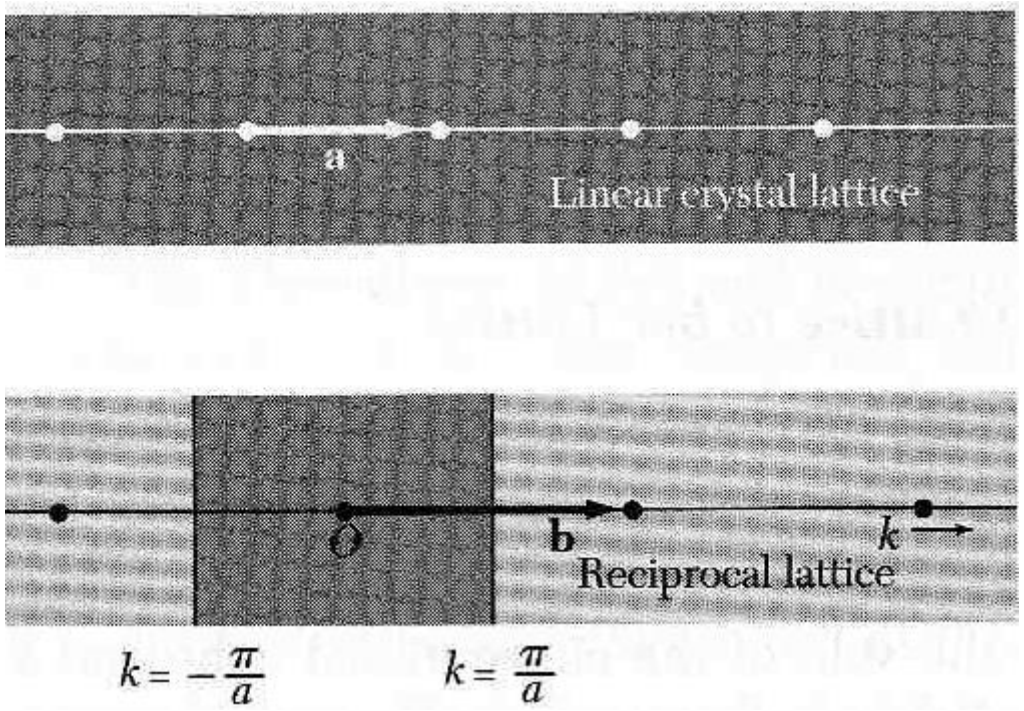


Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is smallest volume about the origin which is bounded entirely by white lines. This square is the Wigner-Seitz primitive cell of the reciprocal lattice. It is called the first Brillouin zone.

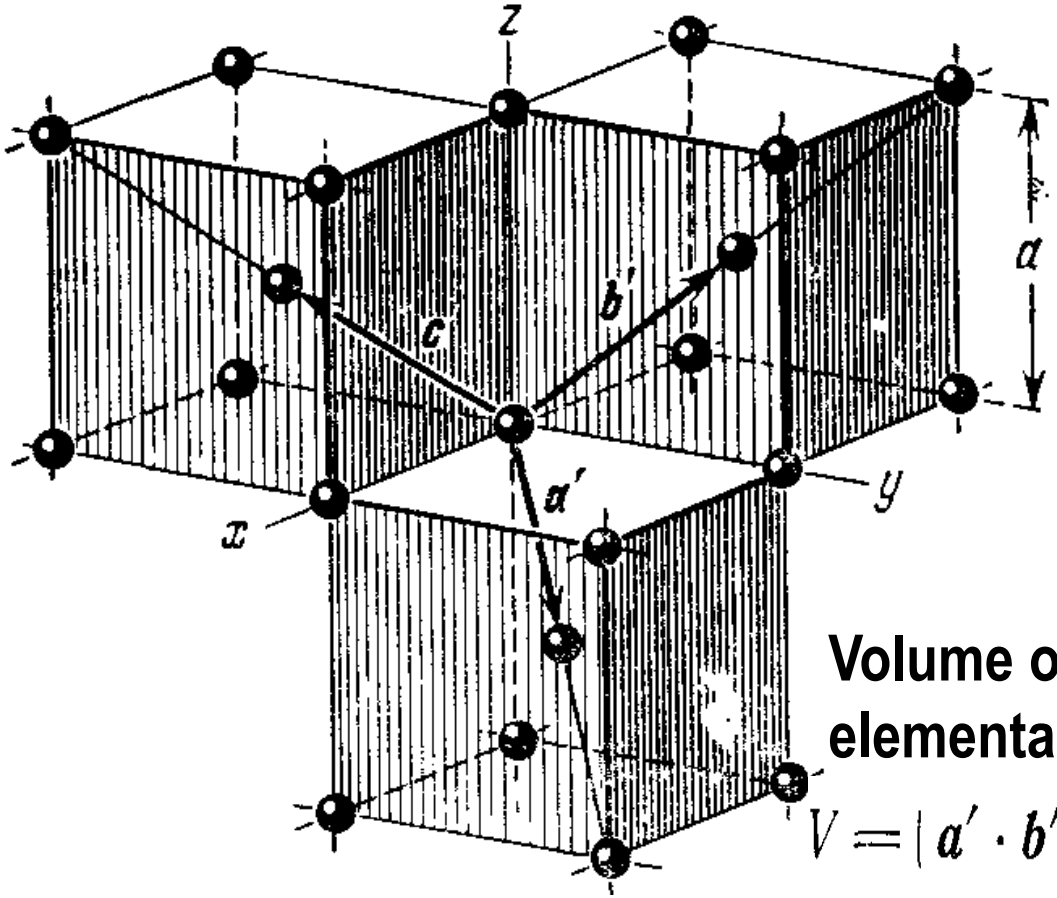
The central cell in the reciprocal lattice is of special importance in the theory of solids, and called the first Brillouin zone. The first Brillouin zone is the smallest volume entirely enclosed by planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

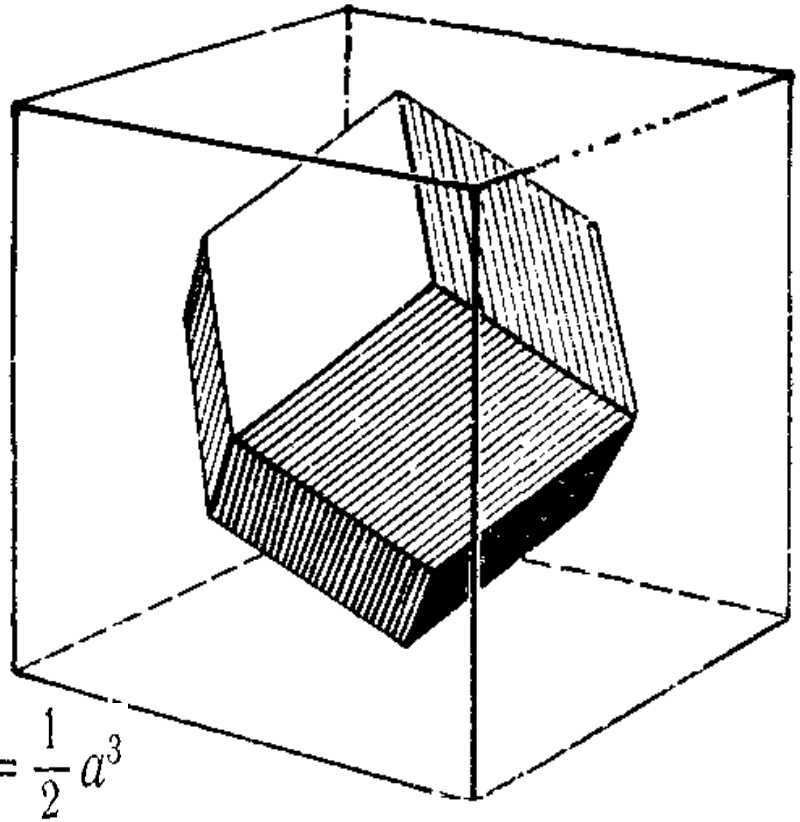


Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from O to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin zone.



Crystal and reciprocal lattices in 1D. The basis vector in the reciprocal lattice is $b=2\pi/a$. The shortest reciprocal lattice vectors from the origin are b and -b. The perpendicular bisectors of these vectors form the boundaries of the first Brillouin zone. The boundaries are at $\kappa = \pm\pi/a$.





Volume of the elementary cell:

$$V = |\, a' \cdot b' \times c' \,| = \frac{1}{2} a^3$$

Primitive basis vectors of the body-centered cubic (BCC) lattice

$$a' = \frac{1}{2} a (\hat{x} + \hat{y} - \hat{z}),$$

$$b' = \frac{1}{2} a (-\hat{x} + \hat{y} + \hat{z}),$$

$$c' = \frac{1}{2} a (\hat{x} - \hat{y} + \hat{z}),$$

First Brillouin zone of the body-centered cubic lattice. Figure is a regular rhombic dodecahedron

Reciprocal lattice vectors of BCC correspond to FCC:

$$A = \frac{2\pi}{a} (\hat{x} + \hat{y}), \quad B = \frac{2\pi}{a} (\hat{y} + \hat{z}), \quad C = \frac{2\pi}{a} (\hat{x} + \hat{z})$$

$$G = hA + kB + lC = \frac{2\pi}{a} [(h + l)\hat{x} + (h + k)\hat{y} + (k + l)\hat{z}]$$

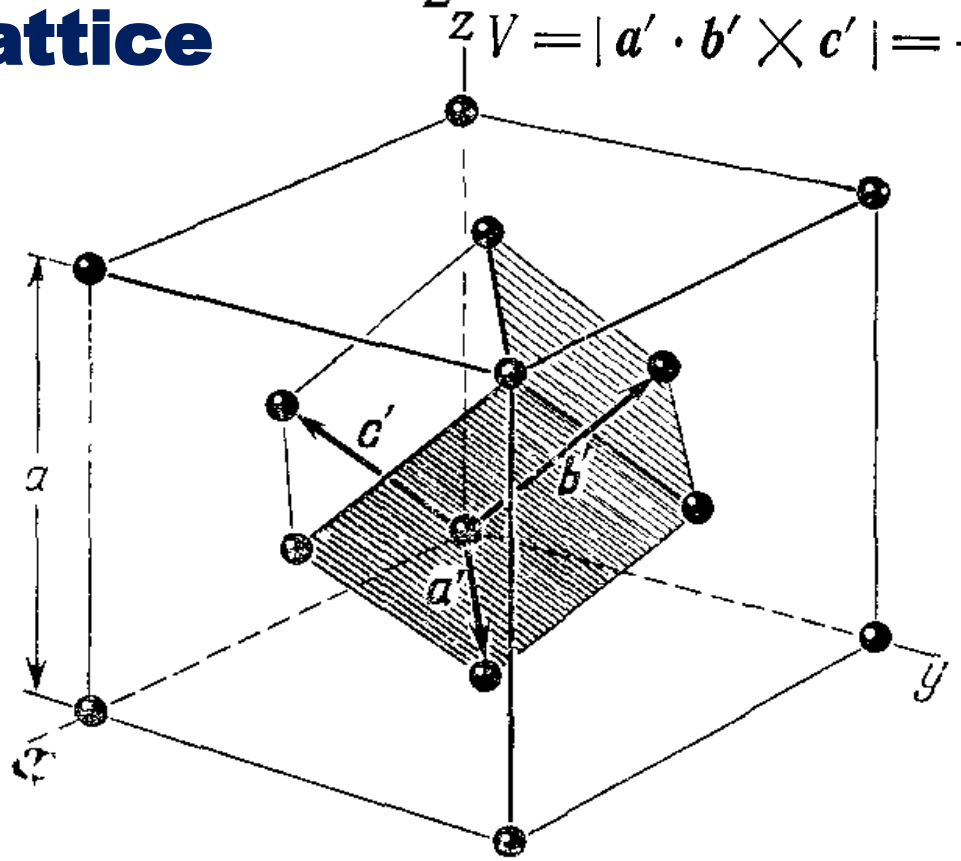
12 shortest vectors of reciprocal lattice:

$$\frac{2\pi}{a} (\pm \hat{x} \pm \hat{y}), \quad \frac{2\pi}{a} (\pm \hat{y} \pm \hat{z}), \quad \frac{2\pi}{a} (\pm \hat{x} \pm \hat{z})$$

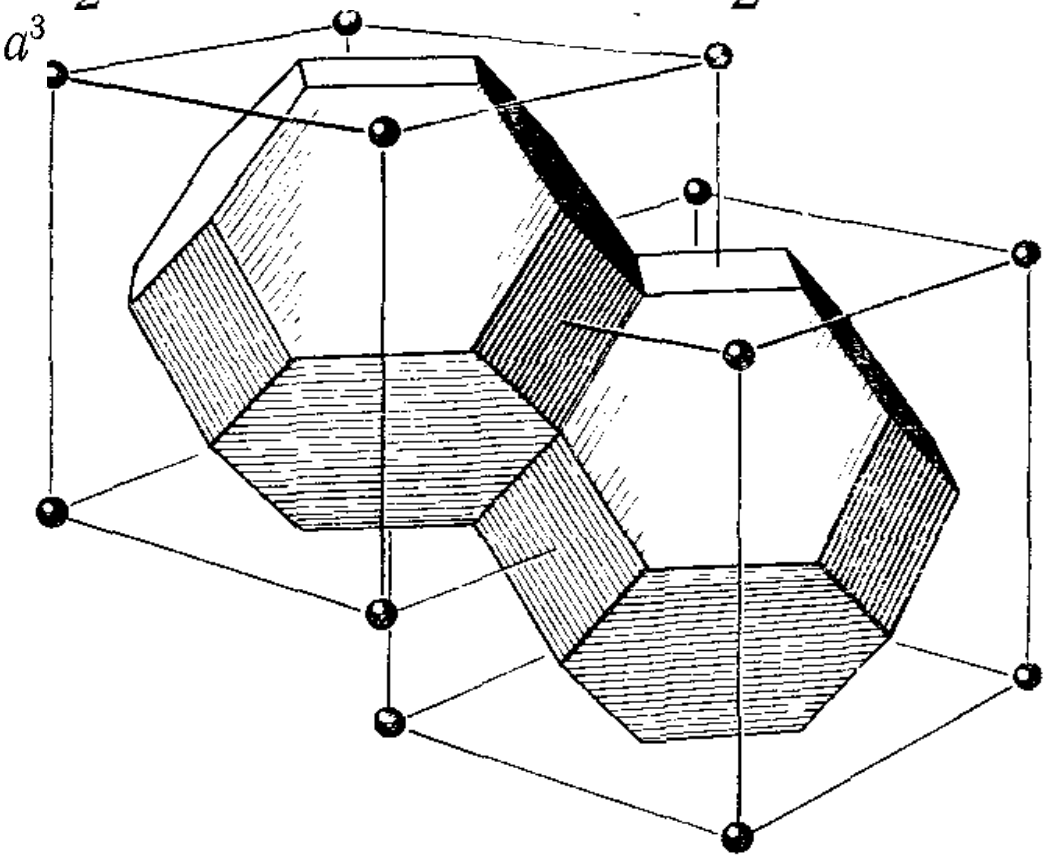
FCC lattice

$$\boldsymbol{a}' = \frac{1}{2}a(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}), \quad \boldsymbol{b}' = \frac{1}{2}a(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}), \quad \boldsymbol{c}' = \frac{1}{2}a(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}}).$$

$$V = |\boldsymbol{a}' \cdot \boldsymbol{b}' \times \boldsymbol{c}'| = \frac{1}{4}a^3$$



Primitive basis vectors of the face-centered cubic (FCC) lattice.



Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

$$\boldsymbol{A} = \frac{2\pi}{a}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}),$$

$$\boldsymbol{B} = \frac{2\pi}{a}(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}), \quad \boldsymbol{G} = \frac{2\pi}{a}[(h-k+l)\hat{\boldsymbol{x}} + (h+k-l)\hat{\boldsymbol{y}} + (-h+k+l)\hat{\boldsymbol{z}}]$$

$$\boldsymbol{C} = \frac{2\pi}{a}(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}).$$

8 shortest vectors: $\frac{2\pi}{a}(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}} \pm \hat{\boldsymbol{z}})$