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X-Ray Diffraction Crystallography

Introduction, Examples and Solved Problems

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With 159 Figures

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Preface

X-ray diffraction crystallography for powder samples is well-established and widely used in the field of materials characterization to obtain information on the atomic scale structure of various substances in a variety of states. Of course, there have been numerous advances in this field, since the discovery of X-ray diffraction from crystals in 1912 by Max von Laue and in 1913 by W.L. Bragg and W.H. Bragg. The origin of crystallography is traced to the study for the external appearance of natural minerals and a large amount of data have been systematized by applying geometry and group theory. Then, crystallography becomes a valuable method for the general consideration of how crystals can be built from small units, corresponding to the infinite repetition of identical structural units in space.

Many excellent and exhaustive books on X-ray diffraction and crystallography are available, but the undergraduate students and young researchers and engineers who wish to become acquainted with this subject frequently find them overwhelming. They find it difficult to identify and understand the essential points in the limited time available to them, particularly on how to estimate useful structural information from the X-ray diffraction data. Since X-ray powder diffraction is one of the most common and leading methods in materials research, mastery of the subject is essential.

In order to learn the fundamentals of X-ray diffraction crystallography well and to be able to cope with the subject appropriately, a certain number of "exercises" involving calculation of specific properties from measurements are strongly recommended. This is particularly true for beginners of X-ray diffraction crystallography. Recent general purpose X-ray diffraction equipments have a lot of inbuilt automation for structural analysis. When a sample is set in the machine and the preset button is pressed, results are automatically generated some of which are misleading. A good understanding of fundamentals helps one to recognize misleading output.

During the preparation of this book, we have tried to keep in mind the students who come across X-ray diffraction crystallography for powder samples at the first time. The primary objective is to offer a textbook to students with almost no basic knowledge of X-rays and a guidebook for young scientists and engineers engaged in full-scale materials development with emphasis on practical problem solving. For the convenience of readers, some essential points with basic equations

are summarized in each chapter, together with some relevant physical constants and atomic scattering factors of elements listed in appendices.

Since practice perfects the acquisition of skills in X-ray diffraction crystallography, 100 supplementary problems are also added with simple solutions. We hope that the students will try to solve these supplementary problems by themselves to deepen their understanding and competence of X-ray crystallography without serious difficulty. Since the field of X-ray structural analysis of materials is quite wide, not all possible applications are covered. The subject matter in this book is restricted to fundamental knowledge of X-ray diffraction crystallography for powder samples only. The readers can refer to specialized books for other applications.

The production of high-quality multi-layered thin films with sufficient reliability is an essential requirement for device fabrication in micro-electronics. An iron-containing layered oxy-pnictide $LaO_{1-x}F_xFeAs$ has received much attention because it exhibits superconductivity below 43 K as reported recently by Dr. Hideo Hosono in Japan. The interesting properties of such new synthetic functional materials are linked to their periodic and interfacial structures at a microscopic level, although the origin of such peculiar features has not been fully understood yet. Nevertheless, our understanding of most of the important properties of new functional materials relies heavily upon their atomic scale structure. The beneficial utilization of all materials should be pursued very actively to contribute to the most important technological and social developments of the twenty-first century harmonized with nature. Driven by environmental concerns, the interest in the recovery or recycling of valuable metallic elements from wastes such as discarded electronic devices will grow significantly over the next decade. The atomic scale structure of various materials in a variety of states is essential from both the basic science and the applied engineering points of view. Our goal is to take the most efficient approach for describing the link between the atomic scale structure and properties of any substance of interest.

The content of this book has been developed through lectures given to undergraduate or junior-level graduate students in their first half (Master's program) of the doctoral course of the graduate school of engineering at both Tohoku and Kyoto universities. If this book is used as a reference to supplement lectures in the field of structural analysis of materials or as a guide for a researcher or engineer engaged in structural analysis to confirm his or her degree of understanding and to compensate for deficiency in self-instruction, it is an exceptional joy for us.

Many people have helped both directly or indirectly in preparing this book. The authors are deeply indebted to Professors Masahiro Kitada for his valuable advice on the original manuscript. Many thanks are due to Professor K.T. Jacob (Indian Institute of Science, Bangalore), Professor N.J. Themelis (Columbia University), Professor Osamu Terasaki (Stockholm University) and Dr.Daniel Grüner and Dr. Karin Söderberg (Stockholm University) and Dr. Sam Stevens (University of Manchester) who read the manuscript and made many helpful suggestions.

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Note: A solution manual for 100 supplementary problems is available to instructors who have adopted this book for regular classroom use or tutorial seminar use. To obtain a copy of the solution manual, a request may be delivered on your departmental letterhead to the publisher (or authors), specifying the purpose of use as an organization (not personal).

Contents

Chapter 1
Fundamental Properties of X-rays

1.1 Nature of X-rays

X-rays with energies ranging from about 100 eV to 10 MeV are classified as electromagnetic waves, which are only different from the radio waves, light, and gamma rays in wavelength and energy. X-rays show wave nature with wavelength ranging from about 10 to 10^{-3} nm. According to the quantum theory, the electromagnetic wave can be treated as particles called photons or light quanta. The essential characteristics of photons such as energy, momentum, etc., are summarized as follows.

The propagation velocity c of electromagnetic wave (velocity of photon) with frequency ν and wavelength λ is given by the relation.

$$c = \nu\lambda \qquad (\mathrm{ms}^{-1}) \tag{1.1}$$

The velocity of light in the vacuum is a universal constant given as $c = 299792458\,\mathrm{m/s}$ ($\approx 2.998 \times 10^8\,\mathrm{m/s}$). Each photon has an energy E, which is proportional to its frequency,

$$E = h\nu = \frac{hc}{\lambda} \qquad (\mathrm{J}) \tag{1.2}$$

where h is the Planck constant ($6.6260 \times 10^{-34}\,\mathrm{J \cdot s}$). With E expressed in keV, and λ in nm, the following relation is obtained:

$$E(\mathrm{keV}) = \frac{1.240}{\lambda(\mathrm{nm})} \tag{1.3}$$

The momentum p is given by mv, the product of the mass m, and its velocity v. The de Broglie relation for material wave relates wavelength to momentum.

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{1.4}$$

The velocity of light can be reduced when traveling through a material medium, but it does not become zero. Therefore, a photon is never at rest and so has no rest mass m_e. However, it can be calculated using Einstein's mass-energy equivalence relation $E = mc^2$.

$$E = \frac{m_e}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} c^2 \tag{1.5}$$

It is worth noting that (1.5) is a relation derived from Lorentz transformation in the case where the photon velocity can be equally set either from a stationary coordinate or from a coordinate moving at velocity of v (Lorentz transformation is given in detail in other books on electromagnetism: for example, P. Cornille, Advanced Electromagnetism and Vacuum Physics, World Scientific Publishing, Singapore, (2003)). The increase in mass of a photon with velocity may be estimated in the following equation using the rest mass m_e:

$$m = \frac{m_e}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \tag{1.6}$$

For example, an electron increases its mass when the accelerating voltage exceeds 100 kV, so that the common formula of $\frac{1}{2}mv^2$ for kinetic energy cannot be used. In such case, the velocity of electron should be treated relativistically as follows:

$$E = mc^2 - m_e c^2 = \frac{m_e}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} c^2 - m_e c^2 \tag{1.7}$$

$$v = c \cdot \sqrt{1 - \left(\frac{m_e c^2}{E + m_e c^2}\right)^2} \tag{1.8}$$

The value of m_e is obtained, in the past, by using the relationship of $m = h/(c\lambda)$ from precision scattering experiments, such as Compton scattering and $m_e = 9.109 \times 10^{-31}$ kg is usually employed as electron rest mass. This also means that an electron behaves as a particle with the mass of 9.109×10^{-31} kg, and it corresponds to the energy of $E = mc^2 = 8.187 \times 10^{-14}$ J or 0.5109×10^6 eV in eV.

There is also a relationship between mass, energy, and momentum.

$$\left(\frac{E}{c}\right)^2 - p^2 = (m_e c)^2 \tag{1.9}$$

It is useful to compare the properties of electrons and photons. On the one hand, the photon is an electromagnetic wave, which moves at the velocity of light sometimes called light quantum with momentum and energy and its energy depends upon

the frequency ν. The photon can also be treated as particle. On the other hand, the electron has "mass" and "charge." It is one of the elementary particles that is a constituent of all substances. The electron has both particle and wave nature such as photon. For example, when a metallic filament is heated, the electron inside it is supplied with energy to jump out of the filament atom. Because of the negative charge of the electron, ($e = 1.602 \times 10^{-19}$ C), it moves toward the anode in an electric field and its direction of propagation can be changed by a magnetic field.

1.2 Production of X-rays

When a high voltage with several tens of kV is applied between two electrodes, the high-speed electrons with sufficient kinetic energy, drawn out from the cathode, collide with the anode (metallic target). The electrons rapidly slow down and lose kinetic energy. Since the slowing down patterns (method of loosing kinetic energy) vary with electrons, continuous X-rays with various wavelengths are generated. When an electron loses all its energy in a single collision, the generated X-ray has the maximum energy (or the shortest wavelength $= \lambda_{\mathrm{SWL}}$). The value of the shortest wavelength limit can be estimated from the accelerating voltage V between electrodes.

$$\mathrm{e}V \equiv h\nu_{\max} \tag{1.10}$$

$$\lambda_{\mathrm{SWL}} = \frac{c}{\nu_{\max}} = \frac{hc}{\mathrm{e}V} \tag{1.11}$$

The total X-ray intensity released in a fixed time interval is equivalent to the area under the curve in Fig. 1.1. It is related to the atomic number of the anode target Z and the tube current i:

$$I_{\mathrm{cont}} = AiZV^2 \tag{1.12}$$

where A is a constant. For obtaining high intensity of white X-rays, (1.12) suggests that it is better to use tungsten or gold with atomic number Z at the target, increase accelerating voltage V, and draw larger current i as it corresponds to the number of electrons that collide with the target in unit time. It may be noted that most of the kinetic energy of the electrons striking the anode (target metal) is converted into heat and less than 1% is transformed into X-rays. If the electron has sufficient kinetic energy to eject an inner-shell electron, for example, a K shell electron, the atom will become excited with a hole in the electron shell. When such hole is filled by an outer shell electron, the atom regains its stable state. This process also includes production of an X-ray photon with energy equal to the difference in the electron energy levels.

As the energy released in this process is a value specific to the target metal and related electron shell, it is called characteristic X-ray. A linear relation between the square root of frequency ν of the characteristic X-ray and the atomic number Z of the target material is given by Moseley's law.

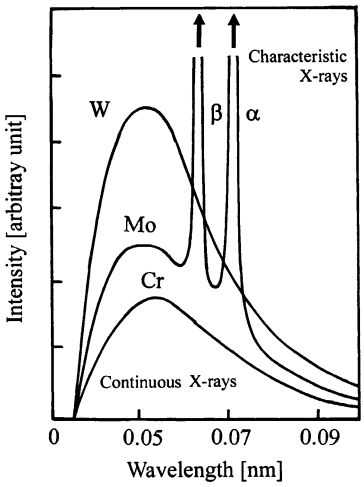

Fig. 1.1 Schematic representation of the X-ray spectrum

$$\sqrt{\nu} = B_{\mathrm{M}}(Z - \sigma_{\mathrm{M}}) \tag{1.13}$$

Here, B_{M} and σ_{M} are constants. This Moseley's law can also be given in terms of wavelength λ of emitted characteristic X-ray:

$$\frac{1}{\lambda} = R(Z - S_{\mathrm{M}})^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.14}$$

Here, R is the Rydberg constant ($1.0973 \times 10^7\,\mathrm{m}^{-1}$), S_{M} is a screening constant, and usually zero for Kα line and one for Kβ line. Furthermore, n_1 and n_2 represent the principal quantum number of the inner shell and outer shell, respectively, involved in the generation of characteristic X-rays. For example, $n_1 = 1$ for K shell, $n_2 = 2$ for L shell, and $n_3 = 3$ for M shell. As characteristic X-rays are generated when the applied voltage exceeds the so-called excitation voltage, corresponding to the potential required to eject an electron from the K shell (e.g., Cu: 8.86 keV, Mo: 20.0 keV), the following approximate relation is available between the intensity of Kα radiation, I_{K}, and the tube current, i, the applied voltage V, and the excitation voltage V_{K}:

$$I_{\mathrm{K}} = B_{\mathrm{S}} i (V - V_{\mathrm{K}})^{1.67} \tag{1.15}$$

Here, B_{S} is a constant and the value of $B_{\mathrm{S}} = 4.25 \times 10^8$ is usually employed. As it is clear from (1.15), larger the intensity of characteristic X-rays, the larger the applied voltage and current.

It can be seen from (1.14), characteristic radiation is emitted as a photoelectron when the electron of a specific shell (the innermost shell of electrons, the K shell) is released from the atom, when the electrons are pictured as orbiting

the nucleus in specific shells. Therefore, this phenomenon occurs with a specific energy (wavelength) and is called "photoelectric absorption." The energy, E_{ej}, of the photoelectron emitted may be described in the following form as a difference of the binding energy (E_B) for electrons of the corresponding shell with which the photoelectron belongs and the energy of incidence X-rays (hν):

$$E_{ej} = h\nu - E_B \tag{1.16}$$

The recoil of atom is necessarily produced in the photoelectric absorption process, but its energy variation is known to be negligibly small (see Question 1.6). Equation (1.16) is based on such condition. Moreover, the value of binding energy (E_B) is also called absorption edge of the related shell.

1.3 Absorption of X-rays

X-rays which enter a sample are scattered by electrons around the nucleus of atoms in the sample. The scattering usually occurs in various different directions other than the direction of the incident X-rays, even if photoelectric absorption does not occur. As a result, the reduction in intensity of X-rays which penetrate the substance is necessarily detected. When X-rays with intensity I_0 penetrate a uniform substance, the intensity I after transmission through distance x is given by.

$$I = I_0 e^{-\mu x} \tag{1.17}$$

Here, the proportional factor μ is called linear absorption coefficient, which is dependent on the wavelength of X-rays, the physical state (gas, liquid, and solid) or density of the substance, and its unit is usually inverse of distance. However, since the linear absorption coefficient μ is proportional to density ρ,(μ/ρ) becomes unique value of the substance, independent upon the state of the substance. The quantity of (μ/ρ) is called the mass absorption coefficient and the specific values for characteristic X-rays frequently-used are compiled (see Appendix A.2). Equation (1.17) can be re-written as (1.18) in terms of the mass absorption coefficient.

$$I = I_0 e^{-\left(\frac{\mu}{\rho}\right)\rho x} \tag{1.18}$$

Mass absorption coefficient of the sample of interest containing two or more elements can be estimated from (1.19) using the bulk density, ρ, and weight ratio of w_j for each element j.

$$\left(\frac{\mu}{\rho}\right) = w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2 + \cdots = \sum_{j=1} w_j\left(\frac{\mu}{\rho}\right)_j \tag{1.19}$$

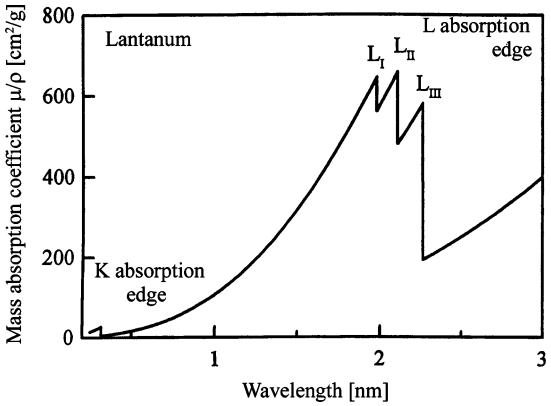

Fig. 1.2 Wavelength dependences of mass absorption coefficient of X-ray using the La as an example

Absorption of X-rays becomes small as transmittivity increases with increasing energy (wavelength becomes shorter). However, if the incident X-ray energy comes close to a specific value (or wavelength) as shown in Fig. 1.2, the photoelectric absorption takes place by ejecting an electron in K-shell and then discontinuous variation in absorption is found. Such specific energy (wavelength) is called absorption edge. It may be added that monotonic variation in energy (wavelength) dependence is again detected when the incident X-ray energy is away from the absorption edge.

1.4 Solved Problems (12 Examples)

Question 1.1 Calculate the energy released per carbon atom when 1 g of carbon is totally converted to energy.

Answer 1.1 Energy E is expressed by Einstein's relation of $E = mc^2$ where m is mass and c is the speed of light. If this relationship is utilized, considering SI unit that expresses mass in kg,

$$E = 1 \times 10^{-3} \times (2.998 \times 10^{10})^2 = 8.99 \times 10^{13} \quad \text{J}$$

The atomic weight per mole (molar mass) for carbon is 12.011 g from reference table (for example, Appendix A.2). Thus, the number of atoms included in 1 g carbon is calculated as $(1/12.011) \times 0.6022 \times 10^{24} = 5.01 \times 10^{22}$ because the numbers of atoms are included in one mole of carbon is the Avogadro's number

(0.6022×10^{24}). Therefore, the energy release per carbon atom can be estimated as:

$$\frac{(8.99 \times 10^{13})}{(5.01 \times 10^{22})} = 1.79 \times 10^{-9} \quad \text{J}$$

Question 1.2 Calculate (1) strength of the electric field E, (2), force on the electron F, (3) acceleration of electron α, when a voltage of 10 kV is applied between two electrodes separated by an interval of 10 mm.

Answer 1.2 The work, W, if electric charge Q (coulomb, C) moves under voltage V is expressed by $W = VQ$. When an electron is accelerated under 1 V of difference in potential, the energy obtained by the electron is called 1 eV. Since the elementary charge e is 1.602×10^{-19} (C),

$$\begin{aligned} 1\text{eV} &= 1.602 \times 10^{-19} \times 1 \qquad \text{(C)(V)} \\ &= 1.602 \times 10^{-19} \qquad \text{(J)} \end{aligned}$$

Electric field E can be expressed with $E = V/d$, where the distance, d, between electrodes and the applied voltage being V. The force F on the electron with elementary charge e is given by;

$$F = eE \qquad \text{(N)}$$

Here, the unit of F is Newton. Acceleration α of electrons is given by the following equation in which m is the mass of the electron:

$$\alpha = \frac{eE}{m} \qquad (\text{m/s}^2)$$

(1) $E = \dfrac{10\,(\text{kV})}{10\,(\text{mm})} = \dfrac{10^4\,(\text{V})}{10^{-2}\,(\text{m})} = 10^6 \quad (\text{V/m})$

(2) $F = 1.602 \times 10^{-19} \times 10^6 = 1.602 \times 10^{-13} \quad (\text{N})$

(3) $\alpha = \dfrac{1.602 \times 10^{-13}}{9.109 \times 10^{-31}} = 1.76 \times 10^{17} \quad (\text{m/s}^2)$

Question 1.3 X-rays are generated by making the electrically charged particles (electrons) with sufficient kinetic energy in vacuum collide with cathode, as widely used in the experiment of an X-ray tube. The resultant X-rays can be divided into two parts: continuous X-rays (also called white X-rays) and characteristic X-rays. The wavelength distribution and intensity of continuous X-rays are usually depending upon the applied voltage. A clear limit is recognized on the short wavelength side.

(1) Estimate the speed of electron before collision when applied voltage is 30,000 V and compare it with the speed of light in vacuum.
(2) In addition, obtain the relation of the shortest wavelength limit λ_{SWL} of X-rays generated with the applied voltage V, when an electron loses all energy in a single collision.

Answer 1.3 Electrons are drawn out from cathode by applying the high voltage of tens of thousands of V between two metallic electrodes installed in the X-ray tube in vacuum. The electrons collide with anode at high speed. The velocity of electrons is given by,

$$eV = \frac{mv^2}{2} \quad \rightarrow \quad v^2 = \frac{2eV}{m}$$

where e is the electric charge of the electron, V the applied voltage across the electrodes, m the mass of the electron, and v the speed of the electron before the collision. When values of rest mass $m_e = 9.110 \times 10^{-31}$ (kg) as mass of electron, elementary electron charge $e = 1.602 \times 10^{19}$ (C) and $V = 3 \times 10^4$ (V) are used for calculating the speed of electron v.

$$v^2 = \frac{2 \times 1.602 \times 10^{-19} \times 3 \times 10^4}{9.110 \times 10^{-31}} = 1.055 \times 10^{16}, \quad v = 1.002 \times 10^8 \text{ m/s}$$

Therefore, the speed of electron just before impact is about one-third of the speed of light in vacuum (2.998×10^8 m/s).

Some electrons release all their energy in a single collision. However, some other electrons behave differently. The electrons slow down gradually due to successive collisions. In this case, the energy of electron (eV) which is released partially and the corresponding X-rays (photon) generated have less energy compared with the energy ($h\nu_{max}$) of the X-rays generated when electrons are stopped with one collision. This is a factor which shows the maximum strength moves toward the shorter wavelength sides, as X-rays of various wavelengths generate, and higher the intensity of the applied voltage, higher the strength of the wavelength of X-rays (see Fig. 1). Every photon has the energy $h\nu$, where h is the Planck constant and ν the frequency.

The relationship of $eV = h\nu_{max}$ can be used, when electrons are stopped in one impact and all energy is released at once. Moreover, frequency (ν) and wavelength (λ) are described by a relation of $\lambda = c/\nu$, where c is the speed of light. Therefore, the relation between the wavelength λ_{SWL} in m and the applied voltage V may be given as follows:

$$\lambda_{SWL} = c/\nu_{max} = hc/eV = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{(1.602 \times 10^{-19})V} = \frac{(12.40 \times 10^{-7})}{V}$$

This relation can be applied to more general cases, such as the production of electromagnetic waves by rapidly decelerating any electrically charged particle including

electron of sufficient kinetic energy, and it is independent of the anode material. When wavelength is expressed in nm, voltage in kV, and the relationship becomes $\lambda V = 1.240$.

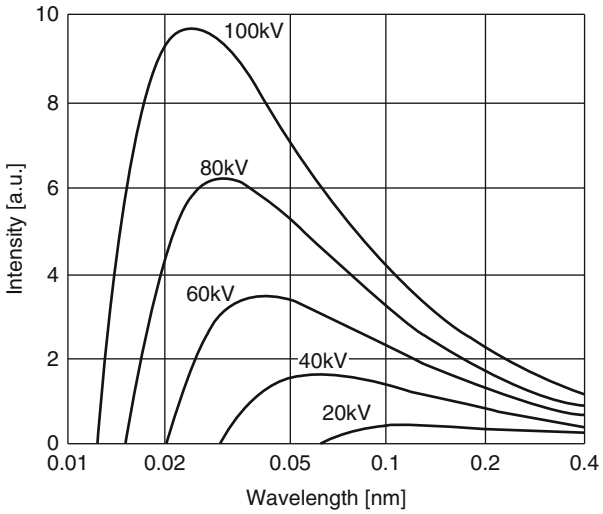

Fig. 1 Schematic diagram for X-ray spectrum as a function of applied voltage

Question 1.4 Kα_1 radiation of Fe is the characteristic X-rays emitted when one of the electrons in L shell falls into the vacancy produced by knocking an electron out of the K-shell, and its wavelength is 0.1936 nm. Obtain the energy difference related to this process for X-ray emission.

Answer 1.4 Consider the process in which an L shell electron moves to the vacancy created in the K shell of the target (Fe) by collision with highly accelerated electrons from a filament. The wavelength of the photon released in this process is given by λ, (with frequency ν). We also use Planck's constant h of (6.626×10^{-34} Js) and the velocity of light c of (2.998×10^{8} ms^{-1}). Energy per photon is given by,

$$E = h\nu = \frac{hc}{\lambda}$$

Using Avogadro's number N_A, one can obtain the energy difference ΔE related to the X-ray release process per mole of Fe.

$$\Delta E = \frac{N_A hc}{\lambda} = \frac{0.6022 \times 10^{24} \times 6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{0.1936 \times 10^{-9}}$$
$$= \frac{11.9626}{0.1936} \times 10^{-7} = 6.1979 \times 10^{8} \quad \text{J/mole}$$

Reference: The electrons released from a filament have sufficient kinetic energy and collide with the Fe target. Therefore, an electron of K-shell is readily ejected. This gives the state of Fe^+ ion left in an excited state with a hole in the K-shell. When this hole is filled by an electron from an outer shell (L-shell), an X-ray photon is emitted and its energy is equal to the difference in the two electron energy levels. This variation responds to the following electron arrangement of Fe^+.

Before release	K1	L8	M14	N2
After release	K2	L7	M14	N2

Question 1.5 Explain atomic density and electron density.

Answer 1.5 The atomic density N_a of a substance for one-component system is given by the following equation, involving atomic weight M, Avogadro's number N_A, and the density ρ.

$$N_a = \frac{N_A}{M}\rho. \tag{1}$$

In the SI system, $N_a\,(\mathrm{m}^{-3})$, $N_A = 0.6022 \times 10^{24}\,(\mathrm{mol}^{-1})$, $\rho(\mathrm{kg/m}^3)$, and $M\,(\mathrm{kg/mol})$, respectively.

The electron density N_e of a substance consisting of single element is given by,

$$N_e = \frac{N_A}{M}Z\rho \tag{2}$$

Each atom involves Z electrons (usually Z is equal to the atomic number) and the unit of N_e is also (m^{-3}).

The quantity $N_a = N_A/M$ in (1) or $N_e = (N_A Z)/M$ in (2), respectively, gives the number of atoms or that of electrons per unit mass (kg), when excluding density, ρ. They are frequently called "atomic density" or "electron density." However, it should be kept in mind that the number per m^3 (per unit volume) is completely different from the number per 1 kg (per unit mass). For example, the following values of atomic number and electron number per unit mass (=1kg) are obtained for aluminum with the molar mass of 26.98 g and the atomic number of 13:

$$N_a = \frac{0.6022 \times 10^{24}}{26.98 \times 10^{-3}} = 2.232 \times 10^{25} \qquad (\mathrm{kg}^{-1})$$
$$N_e = \frac{0.6022 \times 10^{24}}{26.98 \times 10^{-3}} \times 13 = 2.9 \times 10^{26} \qquad (\mathrm{kg}^{-1})$$

Since the density of aluminum is $2.70\,\mathrm{Mg/m}^3 = 2.70 \times 10^3\,\mathrm{kg/m}^3$ from reference table (Appendix A.2), we can estimate the corresponding values per unit volume as $N_a = 6.026 \times 10^{28}\,(\mathrm{m}^{-3})$ and $N_e = 7.83 \times 10^{29}\,(\mathrm{m}^{-3})$, respectively.

Reference: Avogadro's number provides the number of atom (or molecule) included in one mole of substance. Since the atomic weight is usually expressed by the number of grams per mole, the factor of 10^{-3} is required for using Avogadro's number in the SI unit system.

Question 1.6 The energy of a photoelectron, E_{ej}, emitted as the result of photoelectron absorption process may be given in the following with the binding energy E_B of the electron in the corresponding shell:

$$E_{ej} = h\nu - E_B$$

Here, $h\nu$ is the energy of incident X-rays, and this relationship has been obtained with an assumption that the energy accompanying the recoil of atom, which necessarily occurs in photoelectron absorption, is negligible.

Calculate the energy accompanying the recoil of atom in the following condition for Pb. The photoelectron absorption process of K shell for Pb was made by irradiating X-rays with the energy of 100 keV against a Pb plate and assuming that the momentum of the incident X-rays was shared equally by Pb atom and photoelectron. In addition, the molar mass (atomic weight) of Pb is 207.2 g and the atomic mass unit is $1\text{amu} = 1.66054 \times 10^{-27}\,\text{kg} = 931.5 \times 10^3\,\text{keV}$.

Answer 1.6 The energy of the incident X-rays is given as 100 keV, so that its momentum can be described as being $100\,\text{keV}/c$, using the speed of light c. Since the atom and photoelectron shared the momentum equally, the recoil energy of atom will be $50\,\text{keV}/c$. Schematic diagram of this process is illustrated in Fig. 1.

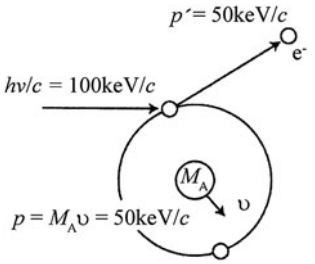

Fig. 1 Schematic diagram for the photo electron absorption process assuming that the momentum of the incident X-rays was shared equally by atom and photoelectron. Energy of X-ray radiation is 100 keV

On the other hand, one should consider for the atom that $1\text{amu} = 931.5 \times 10^3\,\text{keV}$ is used in the same way as the energy which is the equivalent energy amount of the rest mass for electron, m_e. The molar mass of 207.2 g for Pb is equivalent to

207.2 amu, so that the mass of 1 mole of Pb is equivalent to the energy of $207.2 \times 931.5 \times 10^3 = 193006.8 \times 10^3$ keV/c.

When the speed of recoil atom is v and the molar mass of Pb is M_A, its energy can be expressed by $\frac{1}{2}M_A v^2$. According to the given assumption and the momentum described as $p = M_A v$, the energy of the recoil atom, E_r^A, may be obtained as follows:

$$E_r^A = \frac{1}{2}M_A v^2 = \frac{p^2}{2M_A} = \frac{(50)^2}{2 \times (193006.8 \times 10^3)} = 0.0065 \times 10^{-3} \quad \text{(keV)}$$

The recoil energy of atom in the photoelectron absorption process shows just a very small value as mentioned here using the result of Pb as an example, although the recoil of the atom never fails to take place.

Reference:

$$\text{Energy of 1 amu} = \frac{1.66054 \times 10^{-27} \times (2.99792 \times 10^8)^2}{1.60218 \times 10^{-19}} = 9.315 \times 10^8 \quad \text{(eV)}$$

On the other hand, the energy of an electron with rest mass $m_e = 9.109 \times 10^{-31}$ (kg) can be obtained in the following with the relationship of 1 (eV) $= 1.602 \times 10^{-19}$ (J):

$$E = m_e c^2 = \frac{9.109 \times 10^{-31} \times (2.998 \times 10^8)^2}{1.602 \times 10^{19}} = 0.5109 \times 10^6 \quad \text{(eV)}$$

Question 1.7 Explain the Rydberg constant in Moseley's law with respect to the wavelength of characteristic X-rays, and obtain its value.

Answer 1.7 Moseley's law can be written as,

$$\frac{1}{\lambda} = R(Z - S_M)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1}$$

The wavelength of the X-ray photon (λ) corresponds to the shifting of an electron from the shell of the quantum number n_2 to the shell of the quantum number of n_1. Here, Z is the atomic number and S_M is a screening constant.

Using the elementary electron charge of e, the energy of electron characterized by the circular movement around the nucleus charge Ze in each shell (orbital) may be given, for example, with respect to an electron of quantum number n_1 shell in the following form:

$$E_n = -\frac{2\pi^2 me^4}{h^2}\frac{Z^2}{n_1^2} \tag{2}$$

Here, h is a Planck constant and m represents the mass of electron. The energy of this photon is given by,

$$h\nu = E_{n_2} - E_{n_1} = \Delta E = \frac{2\pi^2 me^4}{h^2} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{3}$$

The following equation will also be obtained, if the relationship of $E = h\nu = \frac{hc}{\lambda}$ is employed while using the velocity of photon, c:

$$\frac{1}{\lambda} = \frac{2\pi^2 me^4}{ch^3} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{4}$$

If the value of electron mass is assumed to be rest mass of electron and a comparison of (1) with (4) is made, the Rydberg constant R can be estimated. It may be noted that the term of $(Z - S_M)^2$ in (1) could be empirically obtained from the measurements on various characteristic X-rays as reported by H.G.J. Moseley in 1913.

$$\begin{aligned} R = \frac{2\pi^2 me^4}{ch^3} &= \frac{2 \times (3.142)^2 \times (9.109 \times 10^{-28}) \times (4.803 \times 10^{-10})^4}{(2.998 \times 10^{10}) \times (6.626 \times 10^{-27})^3} \\ &= 109.743 \times 10^3 \,(\mathrm{cm}^{-1}) = 1.097 \times 10^7 \,(\mathrm{m}^{-1}) \end{aligned} \tag{5}$$

The experimental value of R can be obtained from the ionization energy (−13.6 eV) of hydrogen (H). The corresponding wave number (frequency) is 109737.31 cm^{-1}, in good agreement with the value obtained from (5). In addition, since Moseley's law and the experimental results are all described by using the cgs unit system (gauss system), 4.803×10^{-10} esu has been used for the elemental electron charge e. Conversion into the SI unit system is given by (SI unit × velocity of light × 10^{-1}) (e.g., 5th edition of the Iwanami Physics-and-Chemistry Dictionary p. 1526 (1985)). That is to say, the amount of elementary electron charge e can be expressed as:

$$1.602 \times 10^{-19}\mathrm{Coulomb} \times 2.998 \times 10^{10}\,\mathrm{cm/s} \times 10^{-1} = 4.803 \times 10^{-10}\,\mathrm{esu}$$

The Rydberg constant is more strictly defined by the following equation:

$$R = \frac{2\pi^2 \mu e^4}{ch^3} \tag{6}$$

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{m_\mathrm{p}} \tag{7}$$

Here, m is electron mass and m_P is nucleus (proton) mass.The detected difference is quite small, but the value of m_P depends on the element. Then, it can be seen from the relation of (6) and (7) that a slightly different value of R is obtained for each element. However, if a comparison is made with a hydrogen atom, there is a difference of about 1,800 times between the electron mass $m_\mathrm{e} = 9.109 \times 10^{-31}$ kg and the proton mass which is $m_\mathrm{P} = 1.67 \times 10^{-27}$ kg. Therefore, the relationship of (6) is usually treated as $\mu = m$, because m_P is very large in comparison with m_e.

Reference: The definition of the Rydberg constant in the SI unit is given in the form where the factor of $(1/4\pi\epsilon_0)$ is included by using the dielectric constant $\epsilon_0(8.854 \times 10^{-12}\,\mathrm{F/m})$ in vacuum for correlating with nucleus charge Z_e.

$$R = \frac{2\pi^2\mu e^4}{ch^3} \times \left(\frac{1}{4\pi\epsilon_0}\right)^2 = \frac{me^4}{8\epsilon_0^2 ch^3}$$
$$= \frac{9.109 \times 10^{-31} \times (1.602 \times 10^{-19})^4}{8 \times (8.854 \times 10^{-12})^2 \times (2.998 \times 10^8) \times (6.626 \times 10^{-34})^3}$$
$$= \frac{9.109 \times (1.602)^4 \times 10^{-107}}{8 \times (8.854)^2 \times (2.998) \times (6.626)^3 \times 10^{-118}} = 1.097 \times 10^7\,(\mathrm{m}^{-1})$$

Question 1.8 When the X-ray diffraction experiment is made for a plate sample in the transmission mode, it is readily expected that absorption becomes large and diffraction intensity becomes weak as the sample thickness increases. Obtain the thickness of a plate sample which makes the diffraction intensity maximum and calculate the value of aluminum for the Cu-Kα radiation.

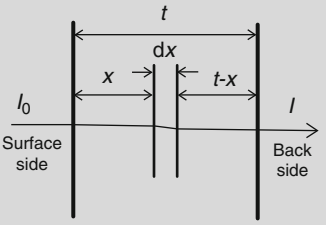

Fig. A Geometry for a case where X-ray penetrates a plate sample

Answer 1.8 X-ray diffraction experiment in the transmission mode includes both absorption and scattering of X-rays. Let us consider the case where the sample thickness is t, the linear absorption coefficient μ, the scattering coefficient S, and the intensity of incident X-rays I_0 as referred to Fig. A.

Since the intensity of the incident X-rays reaching the thin layer dx which is at distance of x from the sample surface is given by $I_0\mathrm{e}^{-\mu x}$, the scattering intensity $\mathrm{d}I'_x$ from the thin layer dx (with scattering coefficient S) is given by the following equation:

$$\mathrm{d}I'_x = SI_0\mathrm{e}^{-\mu x}\mathrm{d}x \tag{1}$$

The scattering intensity $\mathrm{d}I_x$ passes through the distance of $(t - x)$ in the sample and the absorption during this passage is expressed by the form of $\mathrm{e}^{-\mu(t-x)}$. Therefore, the scattering intensity of the thin layer dx after passing through the sample may be given in the following form:

$$\mathrm{d}I_x = (SI_0\mathrm{e}^{-\mu x}\mathrm{d}x)\mathrm{e}^{-\mu(t-x)} = SI_0\mathrm{e}^{-\mu t}\mathrm{d}x \tag{2}$$

The scattering intensity of the overall sample will be equal to the result obtained by integrating the intensity of the thin layer dx with respect to the sample thickness from zero to t.

$$I = \int_0^t SI_0 \mathrm{e}^{-\mu t}\,\mathrm{d}x = SI_0 t \cdot \mathrm{e}^{-\mu t} \tag{3}$$

The maximum value of I is given under the condition of $\mathrm{d}I/\mathrm{d}t = 0$.

$$\frac{\mathrm{d}I}{\mathrm{d}t} = SI_0(\mathrm{e}^{-\mu t} - t\mu \mathrm{e}^{-\mu t}) = 0, \qquad t\mu = 1 \quad \rightarrow \quad t = \frac{1}{\mu} \tag{4}$$

We can find the values of mass absorption coefficient (μ/ρ) and density (ρ) of aluminum for Cu-Kα radiation in the reference table (e.g., Appendix A.2). The results are $(\mu/\rho) = 49.6\,\mathrm{cm}^2/\mathrm{g}$ and $\rho = 2.70\,\mathrm{g/cm}^3$, respectively. The linear absorption coefficient of aluminum is calculated in the following:

$$\mu = \left(\frac{\mu}{\rho}\right)\rho = 49.6 \times 2.70 = 133.92\,(\mathrm{cm}^{-1})$$

Therefore, the desired sample thickness t can be estimated as follows:

$$t = \frac{1}{\mu} = \left(\frac{1}{133.92}\right) = 7.47 \times 10^{-3}\,(\mathrm{cm}) = 74.7\,(\mu\mathrm{m})$$

Question 1.9 There is a substance of linear absorption coefficient μ.

(1) Obtain a simple relation to give the sample thickness x required to reduce the amount of transmitted X-ray intensity by half.
(2) Calculate also the corresponding thickness of Fe-17 mass % Cr alloy (density $= 7.76 \times 10^6\,\mathrm{g/m}^3$) for Mo-K$\alpha$ radiation, using the relation obtained in (1).

Answer 1.9 Let us consider the intensity of the incident X-rays as I_0 and that of the transmitted X-rays as I. Then,

$$I = I_0 \mathrm{e}^{-\mu x} \tag{1}$$

If the condition of $I = \frac{I_0}{2}$ is imposed, taken into account, one obtains,

$$\frac{I_0}{2} = I_{\mathrm{e}}^{-\mu x} \tag{2}$$

$$\frac{1}{2} = \mathrm{e}^{-\mu x} \tag{3}$$

When the logarithm of both sides is taken, we obtain $\log 1 - \log 2 = -\mu x \log e$. The result is $-\log 2 = -\mu x$, as they are $\log 1 = 0$, and $\log e = 1$. Here, natural logarithm is used and the required relation is given as follows:

$$x = \frac{\log 2}{\mu} \simeq \frac{0.693}{\mu} \tag{4}$$

The values of mass absorption coefficients of Fe and Cr for the Mo-Kα radiation are 37.6 and 29.9 cm^2/g obtained from Appendix A.2, respectively. The concentration of Cr is given by 17 mass %, so that the weight ratio of two alloy components can be set as $w_{\mathrm{Fe}} = 0.83$ and $w_{\mathrm{Cr}} = 0.17$. Then, the mass absorption coefficient of the alloy is expressed in the following:

$$\begin{aligned}\left(\frac{\mu}{\rho}\right)_{\mathrm{Alloy}} &= w_{\mathrm{Fe}}\left(\frac{\mu}{\rho}\right)_{\mathrm{Fe}} + w_{\mathrm{Cr}}\left(\frac{\mu}{\rho}\right)_{\mathrm{Cr}} \\ &= 0.83 \times (37.6) + 0.17 \times (29.9) = 36.3\,(\mathrm{cm}^2/\mathrm{g})\end{aligned}$$

Next, note that the unit of the density of the Fe–Cr alloy is expressed in cgs, $7.76 \times 10^6\,\mathrm{g/m}^3 = 7.76\,\mathrm{g/cm}^3$. We obtain,

$$\mu_{\mathrm{Alloy}} = 36.3 \times 7.76\,(\mathrm{cm}^{-1}) = 281.7\,(\mathrm{cm}^{-1})$$

$$x = \frac{0.693}{281.7} = 0.0025\,\mathrm{cm} = 0.025\,\mathrm{mm} = 25\,\mu\mathrm{m}$$

Question 1.10 Calculate the mass absorption coefficient of lithium niobate ($LiNbO_3$) for Cu-Kα radiation.

Answer 1.10 The atomic weight of Li, Nb, and oxygen (O) and their mass absorption coefficients for Cu-Kα radiation are obtained from Appendix A.2, as follows:

	Atomic weight (g)	Mass-absorption coefficient $\mu/\rho\,(\mathrm{cm}^2/\mathrm{g})$
Li	6.941	0.5
Nb	92.906	145
O	15.999	11.5

The molar weight(molar mass) M per 1 mole of $LiNbO_3$ is given in the following:

$$M = 6.941 + 92.906 + (15.999 \times 3) = 147.844\,(\mathrm{g})$$

The weight ratio w_{j} of three components of Li, Nb, and O is to be obtained.

$$w_{\mathrm{Li}} = \frac{6.941}{147.844} = 0.047, \quad w_{\mathrm{Nb}} = \frac{92.906}{147.844} = 0.628, \quad w_{\mathrm{O}} = \frac{47.997}{147.844} = 0.325$$

Then, the mass absorption coefficient of lithium niobate can be obtained as follows:

$$\left(\frac{\mu}{\rho}\right)_{\mathrm{LiNbO_3}} = \sum w_{\mathrm{j}} \left(\frac{\mu}{\rho}\right)_{\mathrm{j}} = 0.047 \times 0.5 + 0.628 \times 145 + 0.325 \times 11.5$$
$$= 94.8\ (\mathrm{cm^2/g})$$

Question 1.11 A thin plate of pure iron is suitable for a filter for Co-Kα radiation, but it is also known to easily oxidize in air. For excluding such difficulty,we frequently utilize crystalline hematite powder (Fe_2O_3:density $5.24\times10^6\ \mathrm{g/m^3}$). Obtain the thickness of a filter consisting of hematite powder which reduces the intensity of Co-Kβ radiation to 1/500 of the Kα radiation case. Given condition is as follows. The intensity ratio between Co-Kα and Co-Kβ is found to be given by 5:1 without a filter. The packing density of powder sample is known usually about 70% of the bulk crystal.

Answer 1.11 The atomic weight of Fe and oxygen (O) and their mass absorption coefficients for Co-Kα and Co-Kβ radiations are obtained from Appendix A.2, as follows:

	Atomic weight (g)	μ/ρ for Co-Kα ($\mathrm{cm^2/g}$)	μ/ρ for Co-Kβ ($\mathrm{cm^2/g}$)
Fe	55.845	57.2	342
O	15.999	18.0	13.3

The weight ratio of Fe and O in hematite crystal is estimated in the following:

$$M_{\mathrm{Fe_2O_3}} = 55.845 \times 2 + 15.999 \times 3 = 159.687$$
$$w_{\mathrm{Fe}} = \frac{55.845 \times 2}{159.687} = 0.699, \quad w_{\mathrm{O}} = 0.301$$

The mass absorption coefficients of hematite crystals for Co-Kα and Co-Kβ radiations are, respectively, to be calculated.

$$\left(\frac{\mu}{\rho}\right)^{\alpha}_{\mathrm{Fe_2O_3}} = 0.699 \times 57.2 + 0.301 \times 18.0 = 45.4\ (\mathrm{cm^2/g})$$
$$\left(\frac{\mu}{\rho}\right)^{\beta}_{\mathrm{Fe_2O_3}} = 0.699 \times 342 + 0.301 \times 13.3 = 243.1\ (\mathrm{cm^2/g})$$

It is noteworthy that the density of hematite in the filter presently prepared is equivalent to 70% of the value of bulk crystal by considering the packing density, so that we have to use the density value of $\rho_f = 5.24 \times 0.70 = 3.67\,g/cm^3$ Therefore, the value of the linear absorption coefficient of hematite powder packed into the filter for Co-Kα and Co-Kβ radiations will be, respectively, as follows:

$$\mu_\alpha = \left(\frac{\mu}{\rho}\right)^{\alpha}_{Fe_2O_3} \times \rho_f = 45.4 \times 3.67 = 166.6\,(cm^{-1})$$
$$\mu_\beta = \left(\frac{\mu}{\rho}\right)^{\beta}_{Fe_2O_3} \times \rho_f = 24.1 \times 3.67 = 892.2\,(cm^{-1})$$

The intensity ratio of Co-Kα and Co-Kβ radiations before and after passing through the filter consisting of hematite powder may be described in the following equation:

$$\frac{I_{Co-K\beta}}{I_{Co-K\alpha}} = \frac{I_0^\beta e^{-\mu_\beta t}}{I_0^\alpha e^{-\mu_\alpha t}}$$

From the given condition, the ratio between I_0^α and I_0^β is 5:1 without filter, and it should be 500:1 after passing through the filter. They are expressed as follows:

$$\frac{1}{500} = \frac{1}{5}\frac{e^{-\mu_\beta t}}{e^{-\mu_\alpha t}} \quad \rightarrow \quad \frac{1}{100} = e^{(\mu_\alpha - \mu_\beta)t}$$

Take the logarithm of both sides and obtain the thickness by using the values of μ_α and μ_β.

$$(\mu_\alpha - \mu_\beta)t = -\log 100 \qquad (\because \log e = 1, \quad \log 1 = 0)$$
$$(166.6 - 892.2)t = -4.605$$
$$t = 0.0063\,(cm^{-1}) = 63\,(\mu m)$$

Question 1.12 For discussing the influence of X-rays on the human body etc., it would be convenient if the effect of a substance consisting of multi-elements, such as water (H_2O) and air (N_2, O_2, others), can be described by information of each constituent element (H, O, N, and others) with an appropriate factor. For this purpose, the value of effective element number $\bar{Z}$ is often used and it is given by the following equation:

$$\bar{Z} = \sqrt[2.94]{a_1 Z_1^{2.94} + a_2 Z_2^{2.94} + \cdots}$$

where $a_1, a_2 \ldots$ is the electron component ratio which corresponds to the rate of the number of electrons belonging to each element with the atomic number