Atomic motion in materials using X-ray

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We will introduce investigation of atomic motion using high resolution inelastic x-ray scattering (IXS) as beamline practical of Cheiron School. The beamline optics for IXS is more complicated than the other beamlines. Scientific field covered with IXS beamline is also too broad to show in this textbook. We will try to show simpler guidance including scientific background through the beamline practical to understand IXS experiment.

Introduction

Atoms in materials do not stay even in solids. Atoms in solids are vibrating at a certain atomic position with keeping structural symmetry. Atomic vibrations in solids are called phonon, which is frequently affected by electronic properties as well as connected with elastic properties in solid state materials. Meanwhile, such atomic vibrations connected with physical properties exist in liquid and gas. One of the contributions of atomic vibration is propagation of sound.

Several experimental techniques have been used in laboratory apparatuses to detect excitations from atomic vibrations: specific heat experiment is applicable to investigation of phonon density of states when electronic contribution is excluded; sonic wave measurements and Brillouin scattering are useful to investigate acoustic phonons through sound velocity; Raman scattering and infrared scattering experiments can detect some optical phonons. Although phonon energy depends on phases of vibrations, these apparatuses are difficult to apply to investigation of phase dependence of phonon energy, phonon dispersion relations.

Phonon dispersion relations were investigated only by inelastic neutron scattering (INS) until about 1990. Soon after inelastic X-ray scattering (IXS) for phonon studies were established [1], third generation synchrotron radiation facilities of ESRF in Europe [2], APS in United States [3] and SPring-8 in Japan [4] were built. One of the difficulties in phonon measurements using X-ray is energy resolution for experiments. This is connected with why INS for phonon
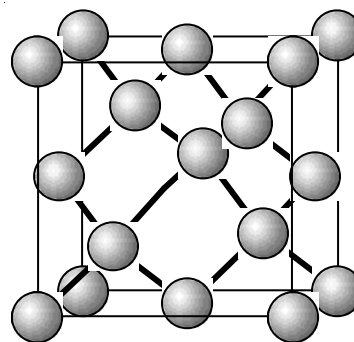

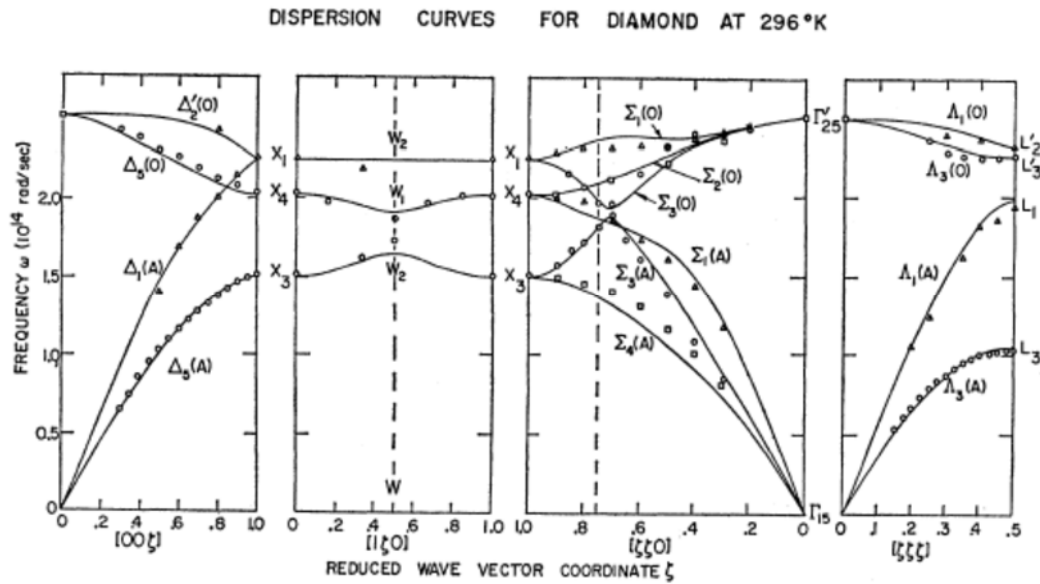Fig. 1. crystal structure of diamond.

Fig. 2. Phonon dispersion relation in diamond. [5]

studies was established by about 40 years earlier than IXS.   Typical energy of phonons is of order of meV or THz.   Figure 1 and 2 show crystal structure of diamond and its dispersion relations obtained by INS, respectively [5].   In addition, wave length required to investigate phonon dispersion relations is comparable to diffraction experiments.

In this beamline practical, we prepared a single crystal sample of a simple metal.   We can know how to measure IXS spectra and polarization effect of IXS spectra, which are useful to carry out IXS to know phonon dispersion in your interesting compounds.

Q1. Why was INS for phonon studies established earlier than IXS?   Discuss differences between IXS and INS on viewpoints of correlation between energy and wave length.

Brief introduction of inelastic X-ray scattering

As mentioned above, meV energy resolution is required in IXS.   To achieve such high energy resolution, higher order reflections from nearly perfect crystals are used as a high resolution monochromator (HRM).   Reflectivity of high order reflections in X-ray is much weaker than that of low order one because of form factor of X-ray scattering.   In addition, signal intensity obtained in most of inelastic experiments is weak.   This means that high brilliant X-ray source is crucial to carry out inelastic scattering experiments.   In addition, reduction of photon flux at HRM should be as small as possible in IXS.   Although several types of HRM's exist to achieve meV resolution, BL35XU chooses a backscattering setup, whose acceptance is large in HRM.

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IXS requires changing energy as well as high energy resolution. The way of changing energy in a backscattering setup is different from that in conventional setups such as a beamline monochromator (e. g. double crystal monochromator). Bragg law gives a relation of $2d \sin\theta = \lambda$, where d denotes space of atomic planes, θ denotes scattering angle and λ denotes wave length of X-ray. Since $\theta \sim 90$ degrees in the backscattering setup, changing scattering angle is not allowed to changing energy unlike a beamline monochromator. Instead of changing scattering angle, space of atomic plane is changed with thermal expansion.

Employment of backscattering optics enlarges beamline size. Figure 3 is layout of BL35XU [6]. There are two reasons why BL35XU is large. One is caused by main beamline optics. The other is caused by analyzer optics. The main beamline optics is located in the backscattering hutch. This consists of offset optics and HRM optics. The former one works for changing beam height to make space around sample area as well as reducing heat load of backscattering monochromator crystal. The latter one works only for reducing the band width of X-ray. To avoid interference of the offset optics and HRM one, a certain space between X-ray beams towards and away of backscattering monochromator is needed. Meanwhile, analyzer optics requires analyzer acceptance as well as backscattering geometry among sample, analyzer crystals and detector elements. As mentioned above, backscattering geometry in X-ray optics is connected with energy resolution. Keeping the backscattering geometry is crucial for high resolution inelastic X-ray scattering. Concerning the analyzer acceptance, BL35XU employs a multi analyzer
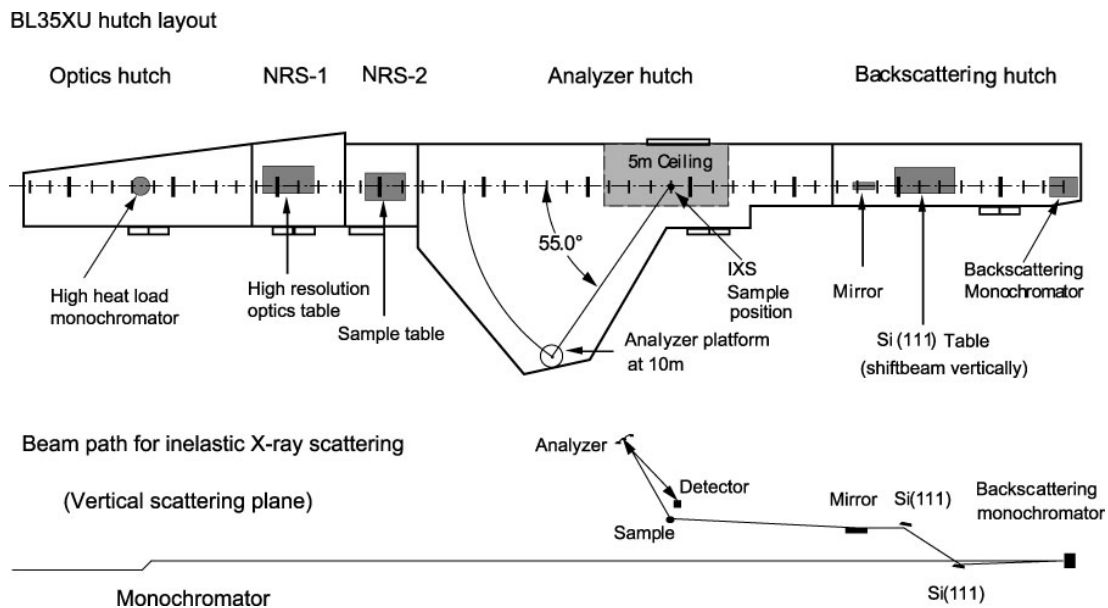

Fig. 3. Layout of inelastic x-ray scattering beamline of BL35XU [6].

system [7]. This system is useful to save time for investigation of phonon dispersion relations because signal intensity of IXS measurement is weak. Details of the multi analyzer system will be explained later.

Q2. Si(n n n) backscattering setup is employed in BL35XU.   The energy resolutions of Si(8 8 8), Si(9 9 9) and Si(11 11 11) setups are 5.5, 3 and 1.5 meV.   How precise temperature control and readout is required in such IXS setups?   The lattice constant of silicon is 0.5431 nm and thermal expansion of silicon is 2.6×10^{-6} K^{-1}.

IXS and INS as a tool for investigation of dynamical structure factor

IXS enables us to investigate dynamical structure factor of materials using X-ray. Since disordered materials such as glasses and liquids have no symmetries, momentum transfer in these materials is scalar. In other words, momentum transfer is determined only by scattering angle for measurements.   Dynamical structure factor depends only on scattering angle.   Then, if you are interested in dynamical structure factor of disordered materials, you will investigate scattering angle dependence of IXS spectra to obtain dynamical structure factor.   On the other hand, since crystalline materials have a certain symmetry based on their own crystal structure, momentum transfer in these materials is a three-dimensional vector.   This means that dynamical structure factor depends on sample orientation as well as scattering angle.

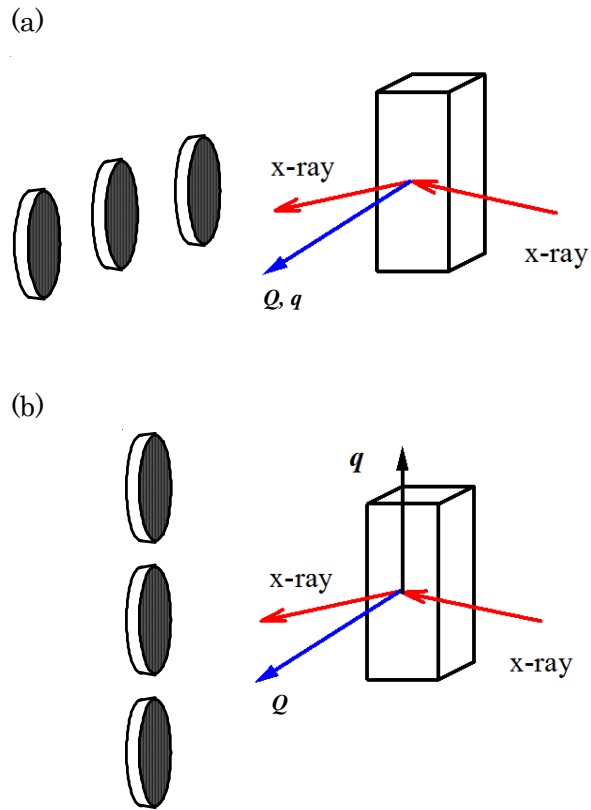Crystalline materials have a translational symmetry. For example,

Fig. 4. Schematic drawing of the relationship between reduced momentum transfer and analyzer location in BL35XU.   (a) Horizontal analyzers can be aligned approximately along the longitudinal direction, and (b) Vertical ones can be aligned approximately along the transverse direction if your sample is mounted properly.

when you are interested in dispersion relations of acoustic modes, you have in principle several choices in reciprocal space, one of which is of course the best position to investigate. Therefore, a standard position to investigate phonon dispersion relation is a Bragg peak, which corresponds to a center of Brillouin zone. To consider momentum transfer Q, existence of translational symmetry is important. Let us consider acoustic modes for simplicity. Now, momentum transfer Q is represented as $\boldsymbol{Q} = \boldsymbol{Q_0} + \boldsymbol{q}$, where Q_0 denotes a center of Brillouin zone and q denotes a reduced momentum transfer in a Brillouin zone. When you choose q parallel to Q_0, you can observe a purely longitudinal acoustic mode; when you choose q perpendicular to Q_0, you observe a purely transverse acoustic mode. If you choose q which is neither parallel nor perpendicular to Q_0, you can observe mixed spectra of longitudinal and transverse modes. This is polarization effect of phonons in IXS and INS.

BL35XU has a 4 x 3 multi-analyzer system [7]. Four horizontal analyzes are located on the scattering plane of the spectrometer. The other eight ones are shifted from the scattering plane. This multi-analyzer system is useful especially for investigation of phonon dispersion relations in crystalline samples. Figure 4 shows schematic drawings for relationships between analyzer arrays and reduced momentum transfer in crystalline samples. If you mount your sample appropriately, you can measure IXS spectra approximately along longitudinal or transverse direction you are interested in. Deviation from ideal reciprocal positions in longitudinal or transverse direction occurs due to lattice constants and structural symmetries of you sample even if you mount and align your sample perfectly.

Comparison with INS

IXS is a complementary technique to INS in investigation of dynamical structure factor based on atomic motions in materials. Since difference between incident energy and scattered one is much larger in IXS than in INS, IXS allows investigation of dynamical structure factor free from kinematic limitation. Then, IXS is a useful technique to investigate atomic dynamics in liquid and glass, which require measurements at high energy and low momentum transfers. In addition, since the beam size at the sample position in IXS is small, say 100 x 100 μm^2 or smaller, IXS is applicable to small samples. Then, if you are interested in a sample under high pressure, using diamond anvil cell for example, you can investigate phonon dispersion relation of the materials in high pressure.

IXS differs from INS in viewpoint of scattering process. Basic scattering process of IXS is Thomson scattering proportionate to number of electrons per each atom. This means scattering intensity in atoms with larger atomic number is stronger. In addition, cross

section of magnetic and/or electronic excitations is too small to detect by IXS. In INS, meanwhile, scattering intensity of atoms is independent of atomic number but depends on nuclear isotope. In addition, cross section of magnetic excitations is comparable to that of phonon excitations in INS. Such differences produce advantages and/or disadvantage of IXS to INS other than sample size and range of momentum transfer. For example, IXS is easy to observe atomic motion of heavy elements and to avoid observation of magnetic excitations.

Q3. What is difference of relationships between energy and momentum transfers in X-ray from that of neutron?

Phonon studies in solid state physics

Phonon dispersion relations reflect elastic properties in material. For example, sound velocities and/or elastic constants in some directions are given by acoustic modes. Instability of crystal structure in materials is also given by phonon dispersion relations. Such instabilities are frequently caused by electronic properties. In other words, phonon dispersion relations are sometimes affected by electronic states through electron-phonon (el-ph) interaction. This reflects one atom binding another neighbor atom with electrons. Kohn anomaly is a phenomenon reflecting el-ph interaction. In materials containing strong electron-phonon coupling, discontinuous phonon dispersion relation caused by Kohn anomaly can be observed at 2 k_F, where k_F is Fermi wave number. Investigation of el-ph coupling in phonon dispersion relations is important to know electronic properties.

References

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