

SITE-SPECIFIC PHONON DENSITY OF STATES MEASURED USING NUCLEAR RESONANT SCATTERING

It is well known that all atoms oscillate in a solid material even at low temperature, and their quantized vibrations are known as phonons. Except for simple materials, different kinds of atoms are usually contained in a material, and the properties of their oscillations are generally not the same. The atomic motion of a certain atom sometimes plays an important role in the characteristics of the material such as the vibration of the impurity or doped atoms in metals or semiconductors, the carrier ion's motions in ionic conductors, and the oscillations of rare-earth atoms in filled skutterudite antimonides. Therefore, each atomic motion provides important information. The nuclear resonant inelastic scattering of synchrotron radiation offers element-(isotope)-specific phonon energy spectra [1]. In this method, the nuclear resonant excitation is attained with synchrotron radiation, the bandwidth of which is reduced to the order of meV, and the energy dependence of the delayed emission from the relatively long-lived excited state yields the inelastic excitation spectrum, i.e., the phonon energy spectrum. Usually, the excitation energy level is inherent to each nucleus and simultaneous excitation of more than two nuclei can be ignored. Therefore, if we tune the incident photon energy around the excitation energy of a certain nuclide, we can obtain the element-specific phonon energy spectrum. However, in the case of compounds with two or more different states of atoms of the same element, such as magnetite, which is a mixed valent Fe compound [2], the observed phonon energy spectrum is the superposition of the partial phonon spectra of individual atoms. Therefore, even this method seems unable to distinguish the "site-specific" phonon energy spectrum. Although the phonon is one of the most fundamental concepts in solids, it was impossible to discern the site-specific atomic motions by previous methods. However, we could use a new method, which is an extension of the nuclear resonant scattering method, and it led to the observation of the site-specific phonons [3]. In general, nuclear energy levels are split and/or shifted owing to the surrounding electronic states; these interactions are small compared to the nuclear excitation energy and known as hyperfine interactions. Because the information of the

individual site through hyperfine interactions is obtained from the incoherent inelastic scattering, we can identify each phonon component of every site by measuring the hyperfine interactions. The effect of hyperfine interactions can be observed in the time evolution of the delayed scattering. Therefore, the measurements of time evolution of the incoherent inelastic scattering at different phonon energies permit us to observe the site-specific phonon energy spectra.

We have performed the measurement of site-specific phonons in magnetite (Fe_3O_4). In magnetite, the iron atoms are located in two nonequivalent positions in the unit cell at room temperature; one-third of the Fe ions (Fe^{3+}) occupy the A sites tetrahedrally coordinated by four oxygen ions and two-thirds of the Fe ions ($\text{Fe}^{2.5+}$) occupy the B sites octahedrally surrounded by six oxygen ions. A polycrystalline sample pressed into the pellet form was used. The measurements were performed at the nuclear resonant scattering beamline **BL09XU** and the JAERI beamline **BL11XU**. The incident radiation was monochromatized to the bandwidth of 3.2 meV (FWHM), and the energy of the radiation was varied around the first nuclear resonant excitation energy of ^{57}Fe (14.413 keV). The scattered 14.413 keV γ rays

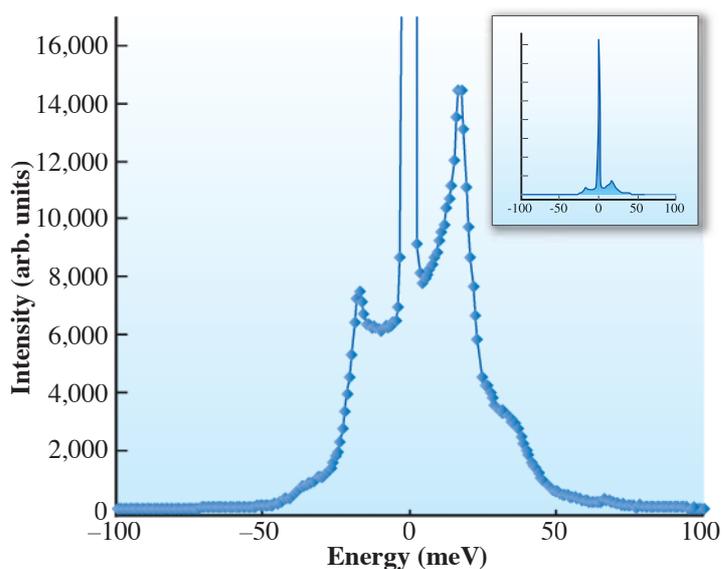


Fig. 1. Energy spectrum of nuclear resonant scattering of all ^{57}Fe atoms in Fe_3O_4 .

at the deexcitation from a resonantly excited nucleus were measured using a multielement Si-avalanche photodiode (APD) detector.

Nuclear resonant inelastic scattering spectrum of ^{57}Fe in Fe_3O_4 is shown in Fig. 1, which is the superposition of the inelastic scattering from both A and B sites. Typical time spectra measured at different incident photon energies are shown in Fig. 2, and the component ratios of A site to B site were obtained at each phonon energy. From a measured nuclear resonant inelastic scattering spectrum (Fig. 1), phonon density of states (PDOS) of all Fe atoms in Fe_3O_4 was reduced and is shown in Fig. 3 as closed circles. Site-specific partial PDOS of A and B sites obtained using the total Fe PDOS and the component ratios in time spectra are shown in Fig. 3 as downward and upward triangles, respectively, and the differences are clearly seen. Around the first peak of 17 meV, the intensity of the B site is larger than that of the A site while their intensities are almost the same at around 35 meV. The observed characteristics indicate their couplings to surrounding atoms, and the phonons at around 17 meV and at around 35 meV are considered to be mainly due to the iron atom's motions and the coupled motions of iron and oxygen atoms, respectively.

We could observe for the first time the partial PDOS identified using the electronic states. This method is applicable not only to solids but also to soft materials and liquids if only their electronic states can be identified in the time spectra. The method allows us to study site-specific phonons in various systems, which we could not access, and will enable the extensive study of the relationships of the electronic states to the local phonon states.

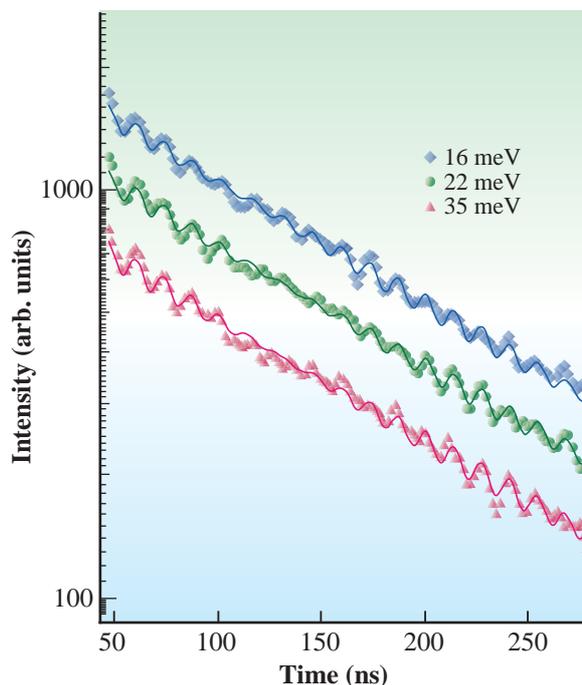


Fig. 2. Time spectra measured at different incident photon energies (deviations from nuclear resonant energy; diamonds: 16 meV, circles: 22 meV, triangles: 35 meV). Lines are least-square fitted spectra with two exponential functions accompanied by sinusoidal quantum beats.

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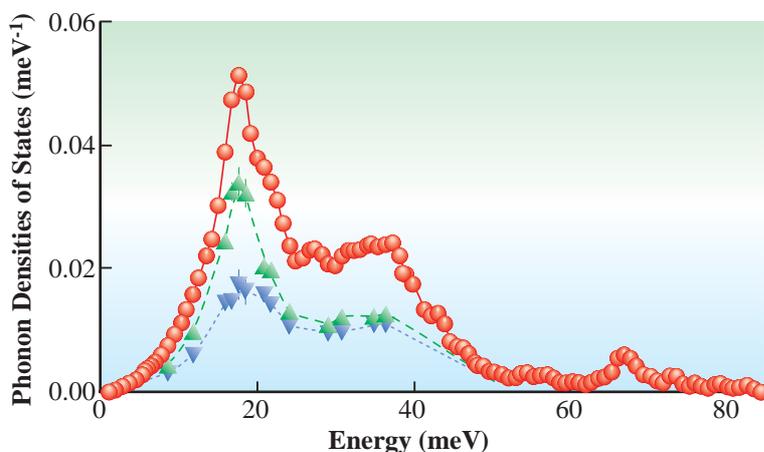


Fig. 3. Phonon densities of states of ^{57}Fe in the Fe_3O_4 sample. The phonon density of states of all Fe is shown in solid circles. The partial phonon densities of states of the A and B sites obtained experimentally are shown as downward and upward triangles, respectively. Lines are guides for the eye.

References

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