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Local vibrational densities of states of dilute Fe atoms in Al and Cu metals

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The local vibrational densities of states of highly dilute Fe (0.017 at. %) in Al metal and Fe (0.1 at. %) in Cu metal were measured by using nuclear resonant inelastic scattering of synchrotron radiation. The characteristic vibrational modes of Fe in Al were found to be modes of resonance with the host Al phonon spectrum. In the measured spectrum of Fe in Cu, in addition to resonance vibrational modes, just above the phonon cutoff energy of Cu metal a peak interpreted as being a localized mode predicted theoretically by the Green's-function method was found.

I. INTRODUCTION

It is widely known that the presence of impurity atoms in a material influences its electronic and/or thermal properties. In the study of these properties, Mössbauer spectroscopy is an effective tool because it allows the characterization of the local surroundings of the impurity atom. In addition to information on the local electronic state, information on the intrinsic dynamic nature of the impurity can be obtained from recoilless fraction measurements.[1] Theoretically, the dynamics of an impurity atom has been studied using the Green's-function technique,[1,2] and theories adopting this technique have been applied to derive the modified vibrational density of states for an impurity atom from the unperturbed phonon density of states. In general, these studies indicate the existence of resonance modes whose frequencies lie in the range of the normal modes of the unperturbed host crystal. Furthermore, in cases where the mass of an impurity atom is sufficiently light and/or the binding of an impurity atom to the host crystal is sufficiently strong, they show that there may be a localized mode, whose frequency is greater than the maximum frequency of the unperturbed crystal. In the case of dilute substitutional Fe atoms in Al metal, the vibrational density of states was expected to be a resonance type from Mössbauer recoilless fraction measurements.[3,4] On the other hand, in the case of dilute substitutional Fe atoms in Cu metal, the existence of a localized mode was predicted,[4,5] but it has not yet been observed.

Though Mössbauer spectroscopy is effective, it is difficult to observe directly the vibrational density of states of an impurity atom, which is exceedingly important in the study of the thermodynamic properties of a material. In cases involving a highly dilute impurity, observation of the vibrational density of states is difficult even by other methods of measurement such as neutron inelastic scattering, with some exceptions. Direct observation is possible, however, by using nuclear resonant inelastic scattering of synchrotron radiation, the applicability and effectiveness of which was shown in Ref. 6. One of the most important features of this method is the possibility of measurement of a specific element and therefore the observation of the intrinsic motion of doped or intercalated atoms is possible.

We have measured the local vibrational spectra of substitutional impurity Fe atoms in Al and Cu metals by using nuclear resonant inelastic scattering and we obtained the impurity vibrational densities of states from the measured spectra. In this paper, we report the results and discuss them by means of the Green's-function method developed by Manheim and co-workers.[7]

II. EXPERIMENT

To prepare an Al-0.017 at. % Fe ($Fe_{0.00017}Al_{0.99983}$) foil specimen, an alloy ingot was made by arc melting a 99.9999% Al foil and metallic ^{57}Fe powder (95.6% enriched) under an argon atmosphere; it was homogenized for 24 h in

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an evacuated tube at 913 K and then quenched in water. By rolling the ingot, the foil was obtained, and it was further homogenized at 913 K in an evacuated tube for 24 h and then quenched in water again. A Cu-0.1 at. % Fe ($Fe_{0.001}Cu_{0.999}$) foil specimen was prepared in a similar manner. An alloy ingot was made by arc melting a 99.999% Cu foil and metallic ^{57}Fe powder (95.54% enriched) under an argon atmosphere; it was homogenized at 1223 K in an argon-hydrogen atmosphere for 24 h and then quenched in water. By rolling the ingot, the foil was obtained, and it was further homogenized at 1223 K in an evacuated tube for 24 h and then quenched in water again. It was confirmed by ^{57}Fe Mössbauer spectroscopy that the Fe atoms were in substitutional sites; the Mössbauer measurements were performed before and after the nuclear resonant inelastic scattering measurements to check the stability of the samples.

The nuclear resonant inelastic scattering experiments were performed at the nuclear resonant scattering beamline (BL09XU) of SPring-8. The storage ring was operated in a special timing mode (14-bunch train×21), having 21 trains each of which has 2-ns-spaced 14 bunches; and the interval between the first bunch of any train and that of the subsequent train is 228 ns. The electron beam current of the storage ring was 70–40 mA at 8 GeV. A double-crystal Si(111) premonochromator was used to handle the high heat load of undulator radiation, and the radiation was monochromatized to the bandwidth of 3.2 meV (full width at half maximum) with a nested high-resolution monochromator consisting of asymmetric Si(5 1 1) and asymmetric Si(9 7 5) channel-cut crystals. The energy of the radiation was varied around the first nuclear resonant energy of $^{57}Fe(14.413\,keV)$. The intensity of the incident beam was monitored with an ionization chamber and a beam flux monitor. The nuclear resonant scattering was observed using a Si-avalanche photodiode (APD) detector with an active area of 25 mm^2.[8] We measured phonon energy spectra as a function of the incident x-ray energy by counting the number of delayed photons at 299 K.

III. RESULTS AND DISCUSSION

The obtained transmission Mössbauer spectra of ^{57}Fe in Al-0.017 at. % Fe and Cu-0.1 at. % Fe foils at room temperature are shown in Figs. 1(a) and (b), respectively. In Al-0.017 at. % Fe, only a resonant absorption singlet is observed and, through least-squares fit of the data to a single Lorentzian curve, the values obtained in estimation of the isomer shift δ with respect to the iron metal at room temperature and the linewidth Γ were 0.43(1) mm/s and 0.25(1) mm/s, respectively. This singlet has already been identified as representing an Fe atom substituted for an Al atom.[9–11] The single line reflects the local cubic symmetry of the substitutional sites, and the near-natural width indicates the uniformity of the local surroundings. In Cu-0.1 at. % Fe, the main component is a singlet and the values of δ and Γ obtained were 0.22(2) mm/s and 0.27(2) mm/s, respectively. In this case also, this singlet has already been identified as representing an Fe atom substituted for a Cu atom.[12] A small quadrupole doublet is, however, observed, adding to the main singlet component, and the values of δ, Γ, and a quadrupole splitting Δ are 0.18(2) mm/s, 0.22(2) mm/s, and 0.63(2) mm/s, respectively. This site is identified as a substitutional Fe atom, with one of the nearest-neighbor Cu atoms substituted by another Fe atom.[12] Since the contribution of this quadrupole doublet is small enough, we ignore this component throughout the following analysis.

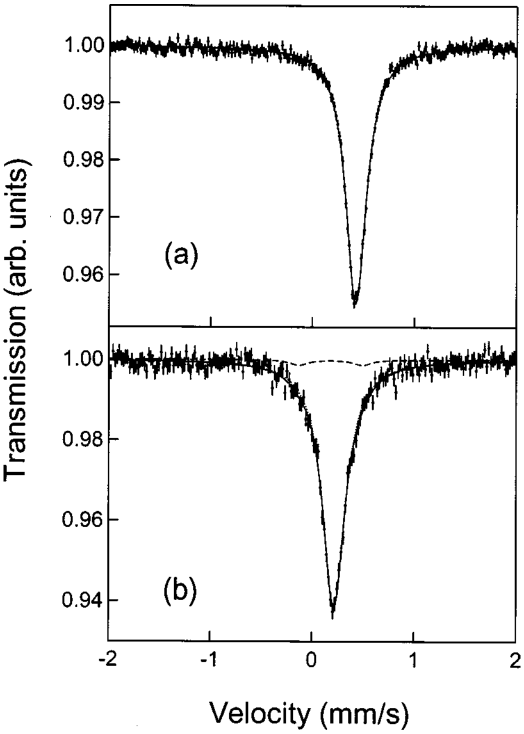

FIG. 1. Transmission Mössbauer spectra of (a) Al-0.017 at. % Fe and (b) Cu-0.1 at. % Fe measured at room temperature. Solid curves in (a) and (b) were obtained through least-squares fit of the data to (a) a singlet Lorentzian curve and (b) singlet and small doublet Lorentzian curves; a singlet represents substitutional Fe atoms surrounded only by host atoms as the nearest neighbors, where a doublet, shown as a dashed curve in (b), represents the small contribution of a substitutional Fe atom with one Fe atom as the nearest neighbor.

Figure 2 shows the nuclear resonant inelastic scattering spectra of ^{57}Fe in (a) Al-0.017 at. % Fe and (b) Cu-0.1 at. % Fe foils. In the case of Al-0.017 at. % Fe, almost all vibrational modes are observed within the energy range of 40 meV, both the phonon creation side (right) and the phonon annihilation side (left). As the phonon cutoff energy of Al metal is 40.3 meV,[13] the character of the vibrational energy spectrum seems to be a resonance type. In the case of Cu-0.1 at. % Fe, most of the vibrational modes are observed within the energy range of 30.6 meV, the value corresponding to the phonon cutoff energy of Cu metal,[14] but, just above the cutoff value, a small contribution is evident.

From the measured spectra, the vibrational densities of states of ^{57}Fe in Al-0.017 at. % Fe and Cu-0.1 at. % Fe were obtained according to the method described in Ref. 15, and these are shown in Figs. 3(a) and 4(a), respectively. The obtained spectra are different from the host phonon densities of states shown in Figs. 3(c) (Ref. 13) and 4(c) (Ref. 14), as expected; the differences are due to the mass difference, and the changes in force constants.

For analysis of the results obtained, we adopted the theory

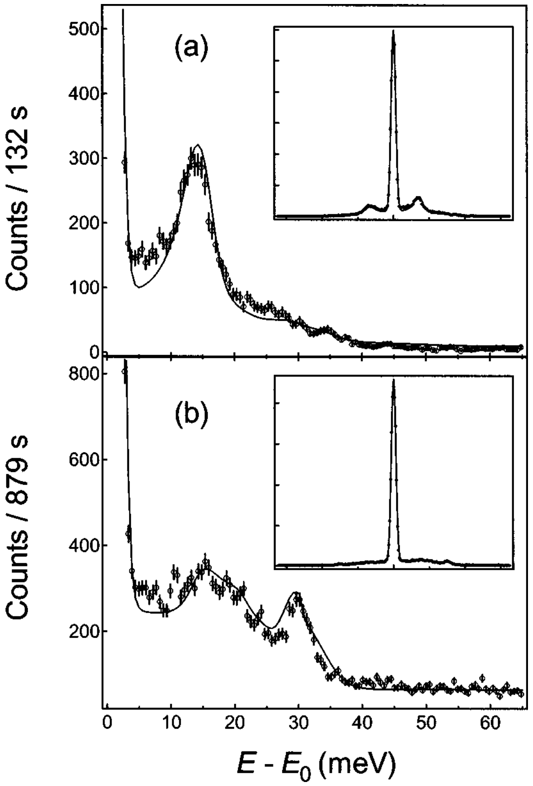

FIG. 2. Nuclear resonant inelastic scattering spectra of synchrotron radiation by ^{57}Fe in (a) Al-0.017 at. % Fe and (b) Cu-0.1 at. % Fe. Solid curves were obtained through least-squares fit of the data to the nuclear resonant excitation cross section σ_r (Refs. 6 and 16) which is calculated on the basis of Mannheim's impurity theory (Refs. 1 and 7) and convoluted with the resolution function of the monochromator; the ratio of the effective host-host force constant to the impurity-host constant was obtained to be 0.94 for (a) Al-0.017 at. % Fe and 0.79 for (b) Cu-0.1 at. % Fe. The incident photon energy and the energy of the first excited state of ^{57}Fe are denoted as E and E_0.

developed by Mannheim and co-workers and Grow *et al.*,[1,7] which applies to an isolated impurity with central forces limited to the first nearest neighbors. This theory has an analytical form and contains only one free parameter A/A' which is the ratio of the host-host force constant to the impurity-host constant. This parameter and the known host-impurity mass ratio M/M' determine the coupling of the impurity to the lattice vibrations of the host metal. The response of the impurity to the phonon density of states of the host $G(\omega)$ is expressed as the modified vibrational density of states $G'(\omega)$ as follows:

$$\begin{aligned}G'(\omega)=&(M/M')G(\omega)\{[1+\rho(\omega)S(\omega)]^2\\&+[(\pi/2)\omega G(\omega)\rho(\omega)]^2\}^{-1}+\delta(\omega-\omega_L)(M/M')\\&\times\{\rho^2(\omega)T(\omega)+(M/M')-[1+\rho(\omega)]^2\}^{-1},\end{aligned}\qquad(1)$$

where

$$\rho(\omega)=(M/M')-1+\omega^2[1-(A/A')]/\mu(+2),\qquad(2)$$

$$S(\omega)=\mathcal{P}\int_0^\infty \omega'^2(\omega'^2-\omega^2)^{-1}G(\omega')d\omega',\qquad(3)$$

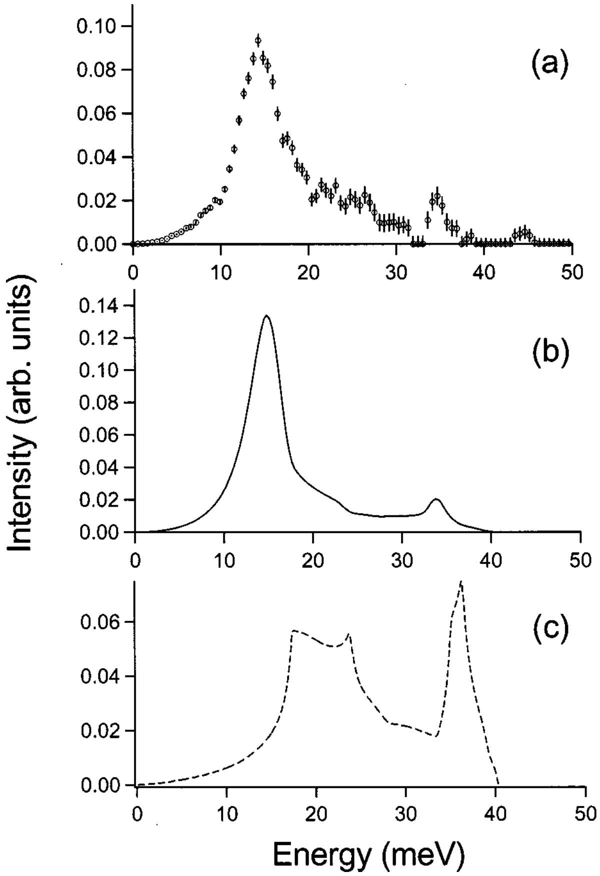

FIG. 3. (a) Vibrational density of states of ^{57}Fe in Al-0.017 at. % Fe obtained from the corresponding measured nuclear resonant inelastic scattering spectrum [Fig. 2(a)]. (b) Response function of the impurity Fe atom to the phonon density of states of Al metal (Ref. 13) calculated on the basis of Mannheim's impurity theory (Refs. 1 and 7); in this calculation, the ratio of the effective host-host force constant to the impurity-host constant was taken to be 0.94. (c) Unperturbed phonon density of states of Al (Ref. 13).

$$T(\omega)=\omega^4\int_0^\infty(\omega'^2-\omega^2)^{-2}G(\omega')d\omega',\qquad(4)$$

$$\mu(n)=\int_0^\infty \omega^n G(\omega)d\omega,\qquad(5)$$

and ω_L denoting a localized mode frequency exists only if it satisfies that $1+\rho(\omega_L)S(\omega_L)=0$ and $\omega_L>\omega_{\max}$; $\delta(\omega-\omega_L)$ is the Dirac δ function and $\mathcal{P}$ stands for principal value. We made the least-squares fit of the data to the nuclear resonant excitation cross section σ_r,[6,16] which is calculated from $G'(\omega)$ and convoluted with the resolution function of the monochromator. For the calculation of $G'(\omega)$ of the dilute substitutional Fe atom in Al and Cu, we used the unperturbed phonon densities of states $G(\omega)$ of Al (Ref. 13) and Cu (Ref. 14), respectively; they were calculated from the results of neutron inelastic scattering experiments. It should be noted that the force-constant ratio A/A' is the effective ratio, since the unperturbed phonon densities of states are obtained based on the results of experiments on neutron inelastic scattering measured at room temperature, and these results may contain anharmonic effects.[17] In the theory, a localized mode has an infinite lifetime and is expressed as a

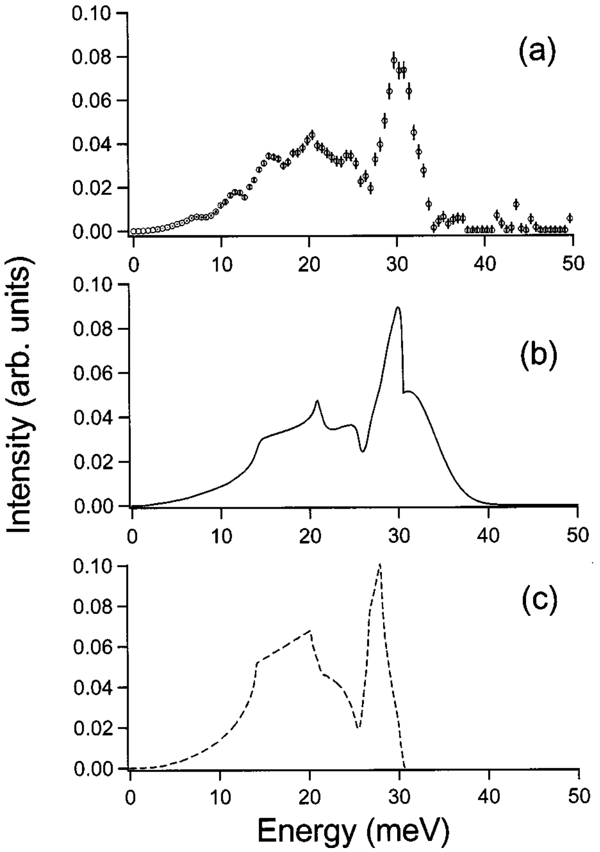

FIG. 4. (a) Vibrational density of states of ^{57}Fe in Cu-0.1 at. % Fe, obtained from the corresponding measured nuclear resonant inelastic scattering spectrum [Fig. 2(b)]. (b) Response function of the impurity Fe atom to the phonon density of states of Cu metal (Ref. 14) calculated on the basis of Mannheim's impurity theory (Refs. 1 and 7); in this calculation, the ratio of the effective host-host force constant to the impurity-host constant was taken to be 0.79. (c) Unperturbed phonon density of states of Cu (Ref. 14).

delta function. In real cases, the localized mode has a finite lifetime owing to anharmonic effects. We assumed, for simplicity, Gaussian broadening only for the localized mode in the least-squares fit provided that it exists. The results of the least-squares fit are shown in Figs. 2(a) and (b) as solid curves, and the obtained effective force constant ratio A/A' was 0.94 (3) for Fe in Al and 0.79 (5) for Fe in Cu. For Fe in Al, the value 1.6 (3) estimated from the recoilless fraction measurement[1] is somewhat larger than our estimated value. On the other hand, the value 0.82 (3) estimated from the recoilless fraction measurement[1] for Fe in Cu is in agreement with our value. Substituting the values we obtained for A/A' in Eq. (1) yields the fitted $G'(\omega)$ of the dilute substitutional Fe atom in Al and Cu shown in Figs. 3(b) and 4(b), respectively. It should be noted that thorough removal of the resolution function from vibrational densities of states obtained experimentally causes errors in the spectra. In our treatment, the partial removal was done using Fourier deconvolution method.[15] For this reason, measured results contain the partially removed (70%) resolution function, but the calculated spectra do not. The resonance character of impurity Fe atoms in Al, expected in view of the considerable mass difference $[M(\mathrm{Al})/M'(\mathrm{Fe})=26.982/57]$, is clearly observed on the vibrational density of states also. In the case of Fe atoms in Cu, to attain a good fit for the vibrational modes around and above the cutoff energy of Cu metal, the existence of a broadened localized mode is required. This localized mode is inherent in Mannheim's theory. In this case, the mass of the impurity Fe atom is slightly lighter than that of the host Cu atom ($M=63.546$), therefore the existence of the localized mode is not surprising and it depends on the force constant for the interaction between the impurity atom and the host atoms. As mentioned above, its existence was predicted on the basis of measurements of the recoilless fraction of the Mössbauer effect, but this has not yet been confirmed. The broadening is thought to be due to anharmonic effects. Regardless of the drastic simplifications in the theory, the reproducibility of the local vibrational densities of states is overall good and therefore the applicability to these impurity systems is proved.

IV. CONCLUSION

We could observe the nuclear resonant inelastic scattering of synchrotron radiation by highly dilute Fe nuclei in Al and Cu metals, and we thereby obtained the local vibrational densities of states. The measured vibrational density of states of Fe in Al shows that the character of the vibrational modes is resonant with host vibrational modes. In the case of Fe in Cu, in addition to resonance vibrational modes, a peak interpreted as being the localized mode predicted by Mannheim's impurity theory was observed. We believe we extended the dilution limit for measurements of the impurity vibrational density of states. As compared to previous recoilless fraction measurements, this method directly provides vibrational densities of states, which is important information pertaining to the thermodynamic properties of materials. Furthermore, our success of the measurements on highly dilute impurity atoms provides the foundations on the study of the impurity system which is not highly dilute and hence is complex. Therefore our results offer some important progress and accelerate the developments in this area of research, and we have a plan to study the impurity ^{57}Fe and/or ^{119}Sn atoms in various metals and/or semiconductors, systematically.

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