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Mechanism of vibrational excitation in inelastic photoemission from solid surfaces

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By using laser-photoemission (LPE) spectroscopy we have investigated inelastic interaction between vibrational modes and photoelectrons emitted from the Cu surfaces. Two plausible rules for vibrational excitation during LPE were obtained. One requires the wave vector matching between the vibrational mode and the electron in the photoexcited state on the surface. The other is that the polarization of the vibrational mode interacting inelastically must lie parallel to the surface plane. These results imply that this inelastic interaction arises dominantly from the resonance scattering and not from the dipole one.

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High-resolution laser-photoemission (LPE) spectroscopy[1–3] is one of the powerful tools to unveil the detailed electronic structure near the Fermi level (E_{F}). For example, the LPE spectroscopy was reported[1] to have a potential for precisely measuring a tiny superconducting gap (~ 1 meV) in f-electron superconductors. The LPE spectra are usually assumed to arise exclusively from the photoelectrons emitted elastically. Inelastic interactions between photoelectrons and vibrations at surfaces are not taken into account in the conventional analysis of the LPE spectra. Contrary to the assumption mentioned above, we have found that the LPE spectra contained vibrationally induced inelastic components.[4–6] The inelastic interaction produces a spectral component whose shape is a replica of the elastic one downshifted by the vibrational energy. The replica has amplitude determined by the inelastic-scattering cross section.

Our experimental finding indicates that this inelastic interaction can alter the photoemission line shape considerably[4–10] particularly near the E_{F}. This implies that the LPE spectra may provide misleading information about the electronic structure, if the influence of the surface vibrational excitation is not taken into account. Thus understanding the mechanism underlying inelastic excitation of vibrational modes by the photoelectron at solid surfaces is crucial in analyzing LPE spectra in detail. Furthermore, deeper understanding of this mechanism should lead to novel applications of the LPE spectroscopy as an alternative method of probing surface vibrations and phonons.

The conditions required for inelastic excitation are well understood as selection rules in the various types of conventional surface vibrational spectroscopy; e.g., infrared reflection absorption spectroscopy (IRAS) and high-resolution electron-energy-loss spectroscopy (HREELS).[11,12] Such selection rules are very important in the analysis of experimental spectroscopic data. This Brief Report describes a spectroscopic study of the dynamics of LPE on the Cu(110) and Cu(001) surfaces. Two propensity rules for vibrational excitation by the photoelectron are obtained through analysis of the observed spectra.

The details of LPE spectroscopy have been described in earlier reports.[4,5,7–10] Briefly, frequency-tripled light from a Ti:sapphire laser was used as the excitation light source. The p-polarized ultraviolet light incident at 54° from the surface-normal excited the photoelectrons. The photoelectrons were measured in the normal-emission geometry using a hemispherical electron-energy analyzer with an energy resolution of 4 meV and an acceptance angle of 1°. The Cu(110) and Cu(001) surfaces were prepared by the standard sputtering and annealing procedures.[13] Exposure of the Cu(110) and Cu(001) surfaces to O_2 at a pressure of 10^{-8} mbar resulted in the formation of the "added row" structure Cu(110)-(2×1)O (Ref. 14) and "missing row" structure Cu(001)-$(\sqrt{2}\times 2\sqrt{2})R45°$O,[15,16] respectively.

Figure 1 shows the LPE spectra of the clean and oxidized Cu surfaces. Since the electronic density of states of the

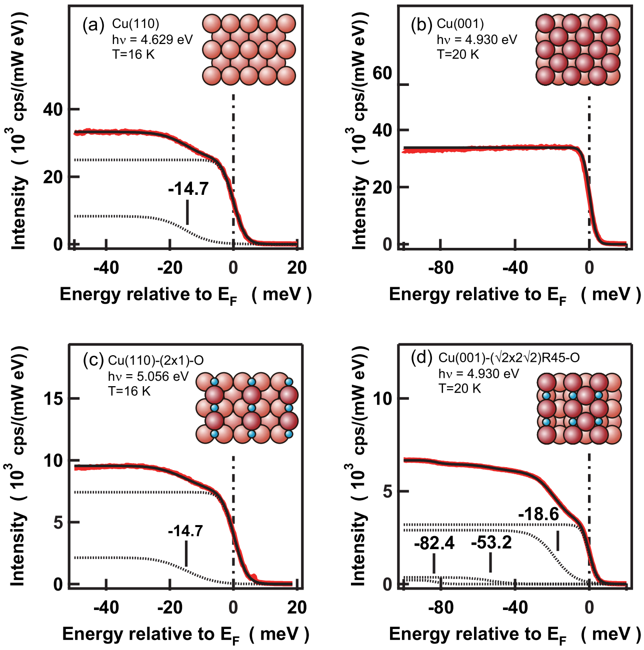

FIG. 1. (Color) LPE spectra of the clean and oxidized Cu(110) [(a) and (c)] and Cu(001) [(b) and (d)] surfaces. The inset shows the atomistic model corresponding to the sample surface. The small and large circles represent O and Cu atoms, respectively. Red curves represent the experimental data. Black solid curves, which closely overlap the red ones, are the results of fit (Ref. 17). The dotted curves represent spectra deconvoluted into the elastic and inelastic components. Vertical bars denote the positions of the step.

TABLE I. Summary of the vibrational mode detected by the laser photoemission spectroscopy experiments.

Sample	Vibrational energy (meV)	Vibrational mode	Polarization with respect to surface
Cu(110)	14.7 ± 1	T_1 phonon	∥
Cu(110)-(2×1)O	14.7 ± 1	T_1 phonon	∥
Cu(001)-$(\sqrt{2}\times2\sqrt{2})R45^\circ$O	18.6 ± 1	T phonon	∥
	53.2 ± 2	Cu-O in-plane vibration (⊥ MR)	∥
	82.4 ± 2	Cu-O in-plane vibration (∥ MR)	∥
Ag(110)	9.1 ± 1	T_1 phonon	∥
Cu(001)-c(2×2)CO [a]	34.6 ± 0.2	Cu-CO FR	∥
	254 ± 2	C-O internal stretching	⊥

[a] References 4–6.

Cu(110) and Cu(001) surfaces are featureless near E_F, the photoemission spectra for both surfaces should be described by the Fermi-Dirac distribution (f_{FD}), if all emission is elastic. However, the shape of the LPE spectrum from the Cu(110) surface deviates significantly from f_{FD} as shown in Fig. 1(a). Figure 1(b) shows that the spectral line shape for the Cu(001) (the red curve) is given by a single f_{FD} (the black curve) while the LPE spectrum of the Cu(110) surface contains a step as can be seen in Fig. 1(a).

The effect of oxidation on the spectral shape is also different for the Cu(110) and Cu(001) surfaces. Figure 1(c) shows that no new step feature appears upon oxidation for the Cu(110) surface, even the energy of the step does not shift. In contrast, at least three new steps appear in the spectrum of the Cu(001)-$(\sqrt{2}\times2\sqrt{2})R45^\circ$O as seen in Fig. 1(d).

To evaluate the inelastic component quantitatively, we decomposed the spectrum into a sum of N individual Fermi-Dirac distribution functions [$N=2$ for the clean and oxidized Cu(110) surfaces and $N=4$ for the Cu(001)-$(\sqrt{2}\times2\sqrt{2})R45^\circ$O surface] as dotted curves shown in Fig. 1. From this procedure, we determined the vibrational energies, which are shown with the vertical bars in Fig. 1 and are summarized in Table I.

Let us discuss the origin of the steps and the excitation mechanism. First, we examine the steps in the Cu(110) and Cu(110)-(2×1)O spectra [Figs. 1(a) and 1(c)]. Since there is no shift in the position of the step upon oxidation, the step must originate from a bulk phonon, not from a surface vibration. Indeed no surface phonon mode at 14.7 meV was observed at the $\bar{\Gamma}$ point by the HREELS and/or the helium atom scattering experiments.[18] To identify the origin of this step, let us examine the bulk electronic and phonon-dispersion curves for Cu along the Γ-K line ([110] direction) shown in Fig. 2.

The initial state of the electron observed in our experiment originates near the Fermi surface. Since the laser photon has essentially zero wave vector, the photoexcited electron has wave vector k_F. In Fig. 2(a), we see that unoccupied electronic states are available at the $\bar{\Gamma}$ point around the vacuum level (E_V), and one of the transverse phonon modes, T_1, has energy 14.3 meV for this wave vector. This energy value resembles to the step energy in Fig. 1(a). We surmise that one of the propensity rules is the wave vector matching between the phonon and the photoexcited electron.

To check the validity of the above rule, we have examined the LPE spectrum of the Cu(001)-$(\sqrt{2}\times2\sqrt{2})R45^\circ$O. The vibrational energy obtained from the spectrum shown in Fig. 1(d) (18.6 meV) is in close agreement with the energy of the transverse (T) phonon mode at k_F along the Γ-X line ([001] direction) as seen in Fig. 2(b).

For further confirmation, we have measured the LPE spectra of the Ag(110) surface. The step in the spectra was observed at 9.1 meV below E_F.[21] This energy of the phonon agrees with the energy of the T_1 mode at k_F along the Γ-K line of Ag.[22,23] These results further confirm that the photoexcited electron interacts inelastically with the phonon mode with matching the wave vector.

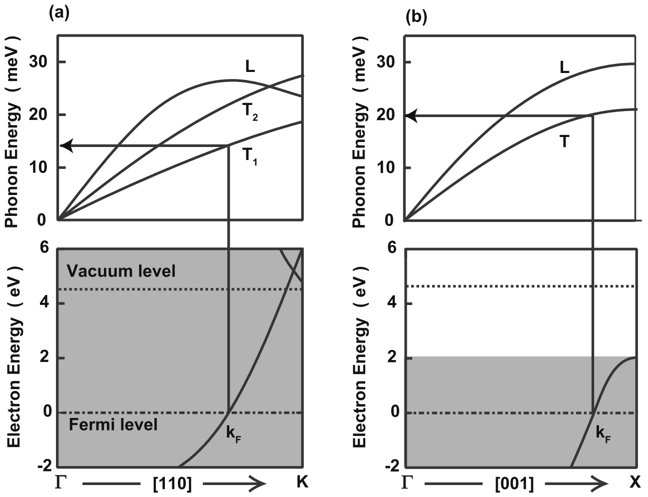

FIG. 2. (a) Bulk phonon (upper) and electronic (lower) dispersion of Cu (Refs. 19 and 20) along the Γ-K line. The shaded area indicates the projected electronic bulk band for the $\bar{\Gamma}$ point of the Cu(110) surface. The transverse phonon propagating along this line in the k space is not degenerate (T_1 and T_2 mode, respectively). The polarization for the T_1 and T_2 mode are parallel to the $[1\bar{1}1]$ and [001] direction, respectively. The horizontal dash-dot and dotted lines denote E_F and E_V of the Cu(110), respectively. (b) Bulk phonon (upper) and electronic (lower) dispersion of Cu along the Γ-X line.

As shown in Fig. 1 the step originating from the bulk transverse phonon was observed in the Cu(001)-($\sqrt{2} \times 2\sqrt{2}$)$R45°$O spectrum but not in the Cu(001) spectrum. This difference does not imply the violation of this propensity rule on the Cu(001) surface. For the Cu(001) surface there is no unoccupied electronic state at E_V for k_F, as shown in Fig. 2(b). And thus the excited electron is emitted directly, without interacting with phonons, into vacuum, where the wave vector of the photoelectron is not k_F at all. On the Cu(001)-($\sqrt{2} \times 2\sqrt{2}$)$R45°$O surface, on the other hand, there are electronic states available at E_V due to the folding of the surface Brillouin zone. Thus, the electron in the excited state can interact with phonons and a step due to such inelastic scattering appears in the spectrum for the Cu(001)-($\sqrt{2} \times 2\sqrt{2}$)$R45°$O.

The requirement for the existence of unoccupied electronic states to reach is also valid for our previous results on the Cu(001)-c(2×2)CO.[4–6] The LPE spectra contained two steps arising from the frustrated rotation (FR) mode and the C-O internal stretching mode. Adsorption of CO on the Cu(001) surface results in the formation of an adsorbate band near E_V.[24] Thus, inelastic scattering due to these two vibrational modes becomes allowed.

Now we consider the propensity rule that depends on the vibrational polarization. As shown in Fig. 1(d) the Cu(001)-($\sqrt{2} \times 2\sqrt{2}$)$R45°$O spectrum contains two additional small steps at 53.2 and 82.4 meV. On the basis of the HREELS data,[15] we can assign the step at 53.2 meV to excitation of the in-plane vibrational mode of the Cu-O bond perpendicular to the missing row (MR), and the step at 82.4 meV to the in-plane vibration parallel to MR. The former is dipole active while the latter is inactive. We note that the Cu-O stretching mode polarized normal to the surface is not observed in the present experiment, although this mode appears as the most intense peak at 36 meV in the HREELS experiments with both the specular and off-specular geometries.[15] As we have noted before, the polarization of the phonons observed in this work is transverse to the surface normal. Table I summarizes the above results in addition to those on the Cu(001)-c(2×2)CO.[4–6] From Table I we see that all the vibrational modes excited during LPE are polarized parallel to the surface plane. We conclude that the vibrational mode polarized parallel to the surface plane is preferentially excited.

The only exception of this rule is the C-O internal stretching mode polarized normal to the surface. This mode appeared as a very weak step in the LPE spectroscopy experiments. At this stage, we do not have sufficient justification for the step concerning the C-O internal stretching mode. The violation implies that the above rule may be less restrictive than the well-known surface-selection rule for IRAS. In addition, the possibility that the tilted CO adsorption due to the surface defect, which leads the parallel polarization, may not be ruled out thoroughly, although the surface is prepared carefully. To understand fully the cause for the violation, further work must be done, both theoretically and on the experimental side including the emission angle dependence.

Here, we consider the proof of the proposed propensity rules for the vibrational excitation during LPE by inspecting the step structures measured by another group. Recently, Ishizaka *et al.*,[2,25] reported repeated stepwise structures in the LPE spectra of heavily boron-doped diamonds. The phonon energy deduced from the step position in their spectra is ~150 meV, which is assigned to the transverse–optical-phonon mode at the Γ point. The heavy doping of boron leads the high electronic density of states around E_F at the Γ point.[26] Thus, the wave vector matching between the phonon and photoexcited electron, which is one of the propensity rules, is operative to their results. In addition, this phonon is known as the Raman-active and IR inactive mode.[27] Taking the symmetry of the diamond into consideration, one recognizes that a vibrational component parallel to the surface plane remains. Therefore, both of these propensities proposed are consistent with their results. In their papers, the cause of the stepwise structure was a variation in photoabsorption based on the Franck-Condon principle. Hence, their conclusion was not compatible with the idea of the inelastic interaction during the LPE. We believe that another experiment (e.g., photoabsorption spectroscopy) is required for a decisive conclusion about the stepwise structures in the LPE spectra of heavily boron-doped diamonds.

Using the propensity deduced from the above considerations, we discuss a possible scenario that will provide a guiding principle to calculating the shape and the intensity of the inelastic component quantitatively. There are three processes for inelastic scattering for the electron at solid surfaces through excitation of vibrational modes;[12] scattering from long-range electric fields (dipole scattering), scattering from the short-range atomic potentials (impact scattering), and scattering through a resonance state (resonance scattering). Only the vibrational mode polarized normal to the surface can be excited in the dipole scattering. This is just opposite to the polarization selection that we have observed above for the vibrational excitation during LPE. Hence, the dipole scattering mechanism is not feasible.

In the impact scattering process the energy dependence of the inelastic-scattering intensity is roughly proportional to the electron energy.[28] However, in the high-energy ($h\nu > 10$ eV) photoemission experiments on Cu surfaces,[19] the inelastic component arising from the vibrational excitation that we have observed in this work were not observed. Therefore, the impact scattering process does not appear to be operative in the vibrational excitation during LPE.

The resonance scattering is a well-documented process in inelastic electron scattering from gas-phase molecules.[29] In this process, the probe electron is trapped temporarily in an affinity level forming a short-lived negative ion. When the probe electron is emitted from the negative ion, the molecule is left in a vibrationally excited state. The resonance scattering can occur from surface atoms and molecules.[30] On the surface, the molecular orbital is perturbed by adsorption. Hence, the affinity level for the free molecule, which is required for the resonance scattering, should correspond to hybridized unoccupied electronic states on the surface. The resonance-scattering process is consistent with our result that the availability of unoccupied states is a prerequisite for vibrational excitation. We believe that resonance scattering is the most feasible process that can account for the vibrational excitation during LPE. Recently vibrational excitation via inelastic electron tunneling in a scanning tunneling microscope junction was described by the resonance scattering.[31–33] It would be very interesting to construct a theory based on resonance scattering, which can account for features in the vibrational excitation during LPE, such as the strong intensity of the inelastic component. The theory would be able to rationalize the experimental results, showing that some vibrational modes [e.g., the T_2 mode for the Cu(110) surface] did not appear in the LPE spectra even though they followed the propensity rule.

In summary, we have investigated the mechanisms underlying the vibrational excitation during LPE. Based on the analysis of LPE spectra from the clean and oxidized Cu surfaces, the following propensity rules are obtained: (i) the wave vector of the scattering vibrational mode must match that of the photoexcited electron; (ii) the polarization of the scattering vibrational mode must lie parallel to the surface plane. The former rule involves the availability of unoccupied states at the energy level in the final state of the photoexcitation (just above E_V in this study). These propensity rules imply that this vibrational excitation during LPE arises dominantly from the resonance scattering. Finally, we point out that the LPE spectroscopy enables us to access surface vibrations that are difficult to detect by the conventional surface spectroscopic tools; e.g., IRAS and HREELS.

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