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Final-state effects on photoemission line shapes at finite temperature

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We have measured angle-resolved photoemission spectra from Al(001) over a large range of temperatures and photon energies. These data were analyzed using a model that allows one to calculate the photoemission intensity for transitions with the simultaneous excitation/absorption of 0, 1, 2, etc., phonons. By making a simple simulation of the line shape, we show that the so-called direct transition (or quasiparticle) peaks always contain a significant contribution from photoemission events with a simultaneous excitation and/or absorption of 1 and 2 phonons, i.e., from transitions that are actually indirect. At low photon energies and/or low temperatures these contributions are small; but as the photon energy or the temperature is raised they increase relative to the elastic or zero-phonon contribution and eventually become the dominant contribution to the so-called direct transition peak. The effect of these phonon-assisted transitions is a significant change of the photoemission line shape. Our model gives a good description of the temperature dependence in the experimental data but only if the phonon-assisted contributions to the photoemission peak are taken into account.

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Recently, much effort has been devoted to the measurement and interpretation of the exact line shapes in angle-resolved photoemission (ARUPS). The reason is that the photoemission intensity measured in ARUPS is closely related to the spectral function of the solid. Therefore this technique has the potential to provide insight into quasiparticle lifetimes as well as into the nonquasiparticle behavior that is found in highly correlated electron systems and for strong electron-phonon coupling.[1] For three-dimensional bulk states, such subtle effects are usually hidden behind the lifetime broadening caused by the uncertainty in $k_\perp$ of the final state. This is much less of a problem in the case of photoemission from electronic surface states[2] and from quasi-two-dimensional materials[3] where the states do not disperse with $k_\perp$. In this paper we show that phonon scattering in the photoemission event can severely change the line shape of a peak because most scattering events involve phonons with a very small momentum and the inelastically scattered electrons are emitted nearly in the same direction and with nearly the same energy as the unscattered electrons. This mechanism should be taken into account when interpreting photoemission line shapes from both bulk and surface states.

The experiment was carried out at the SuperESCA beamline of the electron storage ring ELETTRA in Trieste. Spectra of photoelectrons emitted from the valence band of Al(001) along the surface normal were collected over a wide range of photon energies (165–940 eV) and sample temperatures (133–673 K). The angular resolution was estimated to be close to 2.5°, corresponding to a $\vec{k}_\parallel$ resolution of about 0.3 Å^{-1} at the highest energies shown in this paper. At a photon energy of 194 eV, improving the angular resolution did not lead to a change in the shape of the bulk direct transition peaks within the limit of our experimental accuracy. More details of the experimental procedure will be described elsewhere.[4]

Figure 1 shows the sets of spectra acquired at $h\nu=165$ eV and 567 eV. The main feature in these spectra is the peak at around 11 eV binding energy. This is the so-called direct transition (DT) peak which originates from a direct, i.e., k-conserving, transition from an occupied state along the Γ-X direction of the Brillouin zone to a photoemitted final state along the surface normal. For our investigation, we have chosen to take the direct transition peaks close to the bottom of the band, i.e., close to the Γ point as in Fig. 1, in order to have them well separated from the other peaks that can be found at low binding energies. Note that the name ‘‘direct transition peaks’’ is rather misleading because these peaks also contain considerable contributions from indirect transitions, as we shall see later. The peak at about 3 eV binding energy in the spectra acquired at $h\nu=165$ eV is due to transitions from the Shockley surface state that exists in the gap at the X point of the Brillouin zone.[5] The spectra clearly show a decay of the DT peaks with increasing temperature. It can also be seen that the decay rate changes with the photon energy: at $h\nu=165$ eV the DT peak is still visible even at the highest temperature while at $h\nu=567$ eV it disappears at around 423 K. Similar behavior has been observed for many solids[6] and can be understood qualitatively in terms of a simple model developed by Shevchik.[7] Note that the DT peak also broadens and shifts while decaying. The same behavior is also observed in the rest of the data set, which is not shown here.

We will now analyze the decay of the DT peaks using the model developed in Ref. 8 for the photoemission of valence band electrons including the vibrational degrees of freedom

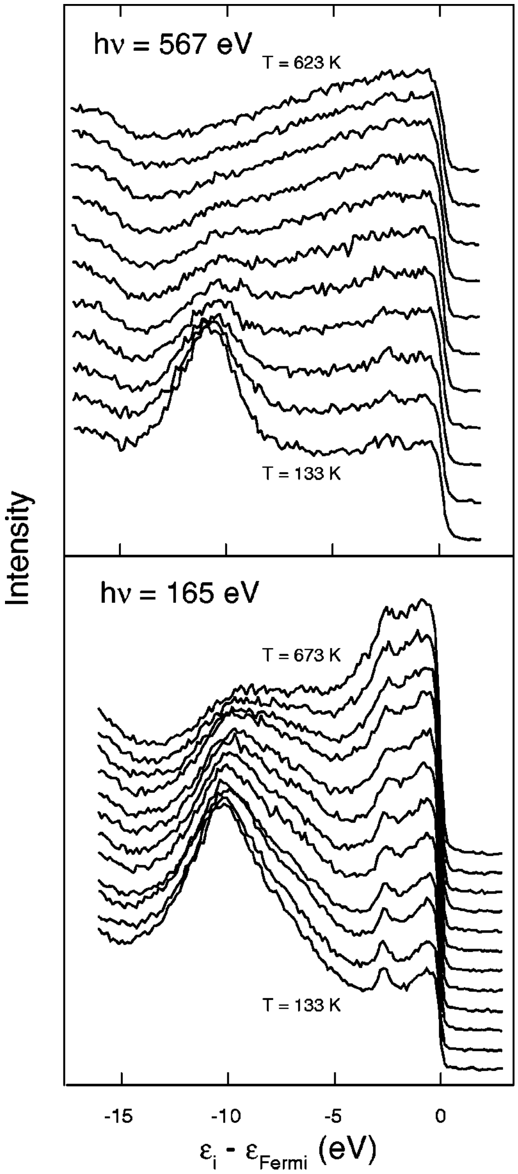

FIG. 1. Spectra of electrons photoemitted from Al(001) along the surface normal at $h\nu = 165$ eV and 567 eV and at several temperatures in the range 133–673 K. The first temperature step is 40 K from 133 K to 173 K; all the following steps are 50 K.

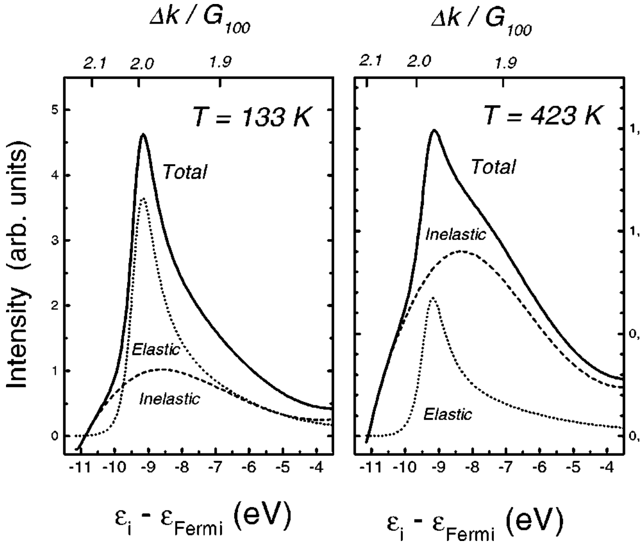

FIG. 2. Calculated spectra corresponding to photoemission from Al(001) along the surface normal at $h\nu = 180$ eV and $T = 133$ and 423 K. The spectra are presented decomposed into the elastic (dotted lines) and inelastic (dashed lines) contributions. The upper scale shows the electron wave vector change in units of the minimum reciprocal lattice vector.

(phonon modes) of the lattice. An important feature of this model is that it allows one to calculate separately the contributions to the intensity of photoemission transitions in which m phonons have been excited and/or absorbed ($m = 0,1,2,\ldots$). The initial state of the electron is composed of two Bloch waves, one propagating toward the surface and one reflected back at the surface, and the final state is the time-reversed low-energy electron diffraction wave function. The lattice vibrations are treated within the Debye model. All the calculations presented in this paper correspond to initial states along the Γ-X line of the bulk Brillouin zone and to emission along the surface normal. The larger vibrational amplitudes at the surface have been taken into account by defining an ''effective'' Debye temperature weighting the layer-dependent Debye temperatures reported in Ref. 9 with exponentials $\exp(-z/\lambda)$, where λ is the electron mean free path and z is the distance from the surface. More details about the model and/or the calculations can be found in Ref. 4 and 8.

Figure 2 shows calculated photoemission spectra in the region of the DT peak, at two different temperatures and decomposed into the elastic ($m = 0$) and inelastic (sum over $m \geqslant 1$) contributions. The main features to be noted in these spectra are that (i) the relative strengths of the elastic and inelastic contributions interchange with the temperature; (ii) the elastic contribution has a sharp peak when $\Delta k_\perp = 2G_{100}$, which is known as the ''third'' Laue condition; and, most importantly, (iii) the inelastic contribution also has a peak close to the initial energies for which the ''third'' Laue condition is fulfilled. Note that this last point causes the line shape of the peak at 423 K to be very different from the elastic line shape: the scattering with phonons does not simply add to the smooth inelastic background under the peak.

To get a better insight into which inelastic transitions form the broad peak of the inelastic intensity, we have plotted the first four contributions to this intensity in Fig. 3. It is seen that (i) the temperature scarcely changes the form of the contributions, only their relative strengths, and (ii) the broad peak is formed essentially by the $m = 1$ and 2 contributions; all the contributions with $m \geqslant 3$ are rather flat in the region of interest and, therefore, contribute mainly to the background under the peak. Thus we conclude that the peak in the calculated spectra in the region of the experimental DT peak is formed not only by the $m = 0$ or elastic contribution, but also by the $m = 1$ and 2 contributions to the inelastic intensity.

In Fig. 4 we have plotted the intensity of the DT peaks in the experimental spectra together with the intensities under the calculated peaks for the same initial states. We show the $m = 0$, 1, and 2 contributions, as well as the sum of these

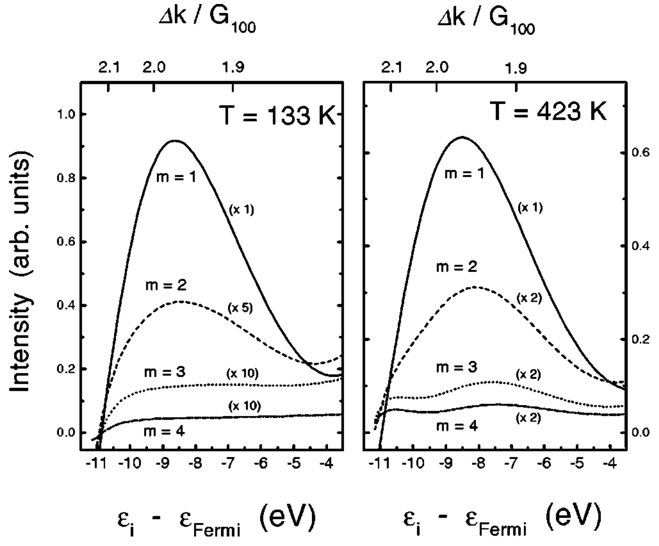

FIG. 3. First four contributions to the inelastic spectra of Fig. 2. *m* is the number of phonons that have been excited and/or absorbed during the photoemission transition. The small negative intensities are caused by the cutoff in the sum over the multiple scattering waves in the final state.

three contributions. The data have been normalized such that this sum and the experimental peak area have a value of unity at the lowest temperature. For both experiment and calculation the intensities have been extracted by integrating the area over a linear background. This simple but consistent way to analyze the data has the advantage that no assumptions about the photoemission line shape have to be made. It is seen that the elastic contribution always falls continuously, whereas the $m=1$ and 2 contributions in many cases first increase with increasing temperature and have a broad maximum. It can be shown, in fact, that each m contribution must reach its maximum strength when $|\Delta\vec{k}|^2\sigma^2 \approx m$, where $\Delta\vec{k}$ is the electron wave vector change during the photoemission transition and σ^2 is the mean square amplitude of vibration of the atoms. This simple formula predicts correctly that the maximum of the $m=1$ contribution should occur at $h\nu = 165$ eV at $T \approx 180$ K and below 100 K at the other photon energies, while that of the $m=2$ contribution should occur at $T \approx 365$ K at $h\nu = 165$ eV, around 160 K at $h\nu = 317$ and 345 eV, and below 100 K at the other photon energies. The main features to be noted in this figure, however, are that the pure elastic contribution (dashed line) decays in all cases faster than the experimental intensity while the sum of the $m=0,1$, and 2 contributions (thick solid line) describes the experimental data rather well. This is consistent with Figs. 2 and 3 and proves that the experimental peak contains considerable contributions from the photoemission events with excitation/absorption of one and two phonons.

The above findings can be explained by the fact that the probability of exciting/absorbing phonons varies inversely with the modulus of the phonon wave vectors.[7] Thus, the photoemission events with excitation and/or absorption of only one or two phonons involve on average a total phonon wave vector small enough for the conservation rules of the electron wave vector to remain valid to a high degree. As the number of phonons exchanged with the lattice increases so does the average total phonon wave vector, and the conservation rules for the electron wave vector gradually relax. Therefore, the $m=1$ and 2 contributions to the inelastic intensity have structures in both the energy and angular distributions similar to those of the $m=0$ contribution, while the contributions with $m \geqslant 3$, being significantly different, simply add up to form the background under the peak.

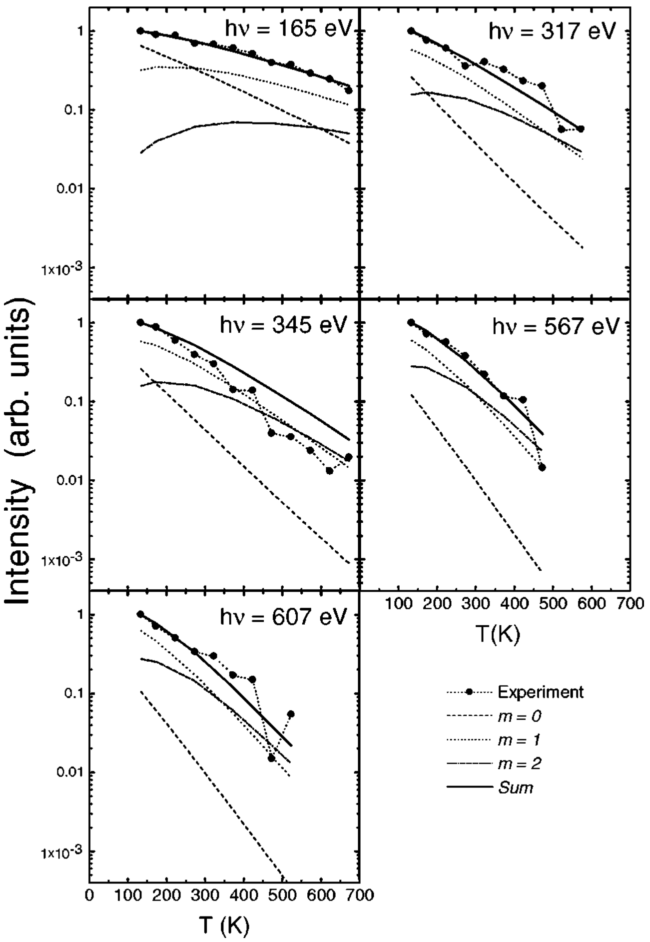

FIG. 4. Plot of the areas of the peaks as a function of temperature. The solid circles correspond to the experimental DT peaks while the other curves are the results of the theoretical calculations.

We have seen that the emission/absorption of phonons during the photoemission event can lead to a severe change of the photoemission line shape. This effect will be especially important when the experimental data are taken at high temperature and/or high photon energies or when the sample has a low Debye temperature. We observe the effect at photon energies that exceed the energies normally used in ARUPS. Note, however, that this does not mean that the phonon scattering can be neglected in an ordinary ARUPS experiment. One has to keep in mind that the momentum transfer for the photoelectron in our experiments is only a factor of 2–4 higher than for a ‘‘normal’’ ARUPS photon energy. The change of line shape also explains the apparent shift and broadening of the DT peak, although this might also be caused by an initial-state effect. Finally, it is evident that the effect depends on the $\vec{k}$ point of the initial state $\vec{k}_i$. If the bands are steep in the vicinity of $\vec{k}_i$ then the broadening effect caused by the phonons will be more severe than in the case of a flat band close to $\vec{k}_i$. In connection with this, one can expect the effect to be less important in the case of a quasi-two-dimensional material because of the fact that the dispersion in one direction is zero. It is perhaps not very surprising that phonon scattering has such a large contribution to the photoemission signal when we recall that even the direct transitions can be achieved only by an umklapp process or, in other words, by scattering with a phonon of zero energy.

In conclusion, we have shown that phonon scattering in a photoemission event can lead to severe changes of the line shape because the so-called direct transition peak also contains contributions from electrons that have actually undergone scattering by one or more phonons. This can be understood by the fact that the most likely scattering happens with phonons close to the Γ point of the Brillouin zone such that the wave vector of the outgoing electron is changed only very little. The line shape changes due to phonon scattering may have general consequences for the interpretation of photoemission data in terms of a spectral function.

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