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Nonlifetime effects in photoemission linewidths

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The intrinsic linewidth in angle- and energy-resolved photoemission is generally assumed to be limited by the final-state lifetime. High-resolution measurements of the intrinsic linewidths for emission from bulk and surface states of Cu show that in some cases the linewidth is dominated by weakened $k_{||}$ conservation. We tentatively attribute this effect to a finite mean free path for *elastic* scattering from the small number (≈ 0.01 monolayer) of impurities present at the surface. This suggests that as instrumental precision improves, sample preparation may be the limiting factor determining resolution.

I. INTRODUCTION

In recent years angle- and energy-resolved photoemission has progressed to the point where resolution is often limited, not by experimental linewidth, but by intrinsic mechanisms such as final-state lifetimes. The possibility therefore exists to study final-state lifetimes directly by photoemission; several such studies have recently been reported.[1-5]

The analysis in these studies has in every case been based on a crucial assumption—that the wave vector $\vec{k}$ (or at least its component $k_{||}$ parallel to the surface) remains a good quantum number, while energy conservation is weakened because of the finite lifetime of the final (excited) state. Formally, this amounts to assuming that the self-energy tensor $\Sigma_{kk'}(\omega)$ is diagonal but complex.

Here we report results of two experiments which clearly demonstrate that weakened conservation of wave vector $k_{||}$ may dominate the observed linewidth. An interpretation based strictly on lifetime-induced energy broadening is seen to yield unphysical and even inconsistent results, while including possible $k_{||}$ broadening in the analysis yields consistent and sensible results for both the intrinsic lifetime and $k_{||}$ broadening. Such an analysis amounts to allowing off-diagonal elements in $\Sigma_{kk'}$.

The first experiment, which has been briefly described elsewhere,[6] measures the linewidth for emission from a surface state on Cu(111). If $k_{||}$ were truly conserved, the intrinsic linewidth should be equal[6] simply to the final-state hole inverse lifetime Γ_h, which vanishes at the Fermi level (E_F). (For notational simplicity we take $\hbar = 1$.) The observed linewidth, however, *increases* as the state disperses towards E_F.

The second experiment measures the final-state electron lifetime for bulk emission from a state near E_F with the use of an experimental configuration employed previously by Grepstad.[1] We find that the *apparent* lifetime of a bulk state varies drastically depending upon crystal surface orientation. This absurd result is easily corrected by including the effects of weakened $k_{||}$ conservation.

Most important, both experiments, with the use of two different crystals cut from the same boule and prepared using standard techniques, yield almost identical values for the $k_{||}$ intrinsic "linewidth" $\Delta k_{||} \approx 0.03$ Å^{-1} [full width at half maximum (FWHM)], suggesting an elastic mean free path of roughly 30 Å.

In analyzing our results, weakened $k_{||}$ conservation is described by a phenomenological parameter Δk, which is best viewed as an inverse elastic mean free path; it is quite analogous to the inverse lifetime Γ. Note, however, that the final-state lifetime *already* implies a mean free path $v\Gamma^{-1}$; Δk describes only additional (nonlifetime) contributions to the mean free path (e.g., impurity and defect scattering). Unfortunately, the effects of finite mean free path are identical to those of finite angular resolution. Below and elsewhere we describe the tests which establish that the effect is not an instrumental artifact but is consistent with possible impurity scattering by the extremely small (≈ 0.01 monolayer) surface contamination present. Thus, in the future, sample preparation rather than instrumental precision may be the limiting factor in experimental resolution.

II. EXPERIMENT

The experiments were performed in a new photoemission spectrometer which is described in detail elsewhere.[7] The heart of this system is a 50-mm mean-radius hemispherical deflection analyzer which has been optimized for very high angular and energy-resolution studies. The energy resolution is variable down to 20 meV, while the angular resolution can be varied between $0.3° \leq \Delta\theta \leq 1.3°$, where $\Delta\theta$ is the FWHM of the triangular resolution function. Since in these experiments we wish to measure natural peak widths, it is important to eliminate all experimental contributions to measured widths. The relevance of experimental energy resolution in this regard is obvious, but for the rapidly dispersing *sp*-derived states sampled in this study, finite angular or momentum resolution can also increase the observed peak width.[4,6] The best procedure for determining the natural width is to measure the width as a function of energy and angular resolution and then to extrapolate both to zero.[6,7] This is better than those procedures which involve Gaussian[4] or Lorentzian[3] deconvolutions since analyzer response functions never have such a well-defined character. In general, we follow such an extrapolation here with limitations dictated by the natural width and dispersion of the peak under study.

Cu(001) and Cu(111) crystals were spark-cut and pol-

ished by standard techniques to within 0.5° of the appropriate axis. They were then installed in the spectrometer, and following several cycles of neon-ion sputtering and annealing to 800 K, the crystals' surfaces had less than 1% of a monolayer contamination as determined by Auger spectroscopy. Good crystalline quality was indicated by sharp low-energy electron-diffraction (LEED) spots. With the use of the electron spectrometer, the width of the (00) LEED beams were determined to be less than 1° for both crystals. Photoemission experiments were performed using Ar I, Ne I, and He I resonance radiation incident on the surface at an angle of 45° from the normal in the ΓLUX plane of the bulk Brillouin zone. Energy-distribution curves (EDC's) were collected in this plane by rotating the energy analyzer in vacuum. Angular alignment to within 0.5° was assured by laser autocollimation, *in situ* electron diffraction, and by assuming symmetry of experimental dispersion relations about symmetry points.

III. RESULTS

A. Cu(111) surface-state lifetime

This section presents high-resolution angle-resolved photoemission (ARP) data on the well-known[8,9] *sp*-like surface state of Cu(111), which yield the surprising result that the linewidth for this state *increases* on approaching the Fermi level (E_F). The hole decay rate, and hence the linewidth, are, however, expected to go to zero at E_F due to the vanishing phase space for Auger decay. Some typical spectra are shown in Fig. 1. Broadening of the surface-state peak as it approaches E_F is clearly visible.

The surface-state peak in Fig. 1 can be fitted with a Lorentzian convoluted with the Fermi function, yielding peak energy and linewidth as a function of $k_{||}$. Figure 2 shows the energy dispersion of the state along with the projected bulk continuum. A least-squares analysis yields the parabolic fit $E=8.25k_{||}^2-0.389$, with E in eV and $k_{||}$ in Å^{-1}. (The bulk continuum edge was calculated assuming a parabolic fit to Fermi-surface data[10] and to the measured energy[3] at $L_{2'}$.)

Both the energy and angular resolution were independently varied. The inset in Fig. 2 shows the linewidth versus $k_{||}$ for two settings of the analyzer $k_{||}$ resolution, which we denote Δk_x. The analyzer energy resolution in these data is 20 MeV (all widths are FWHM). Two features are immediately apparent. The linewidth increases on approaching k_F and this increase is approximately linear with $k_{||}$.

Four factors contribute to the surface-state linewidth: the experimental energy resolution Γ_x, the intrinsic (hole-lifetime) width Γ_0, the experimental $k_{||}$ resolution Δk_x, and the intrinsic $k_{||}$ width Δk_0, which may be nonzero due to scattering by defects, impurities, etc. The last factor, Δk_0, has never to our knowledge been considered in the interpretation of experimental data.[11] If the instrumental line shapes were Lorentzian, as are the intrinsic

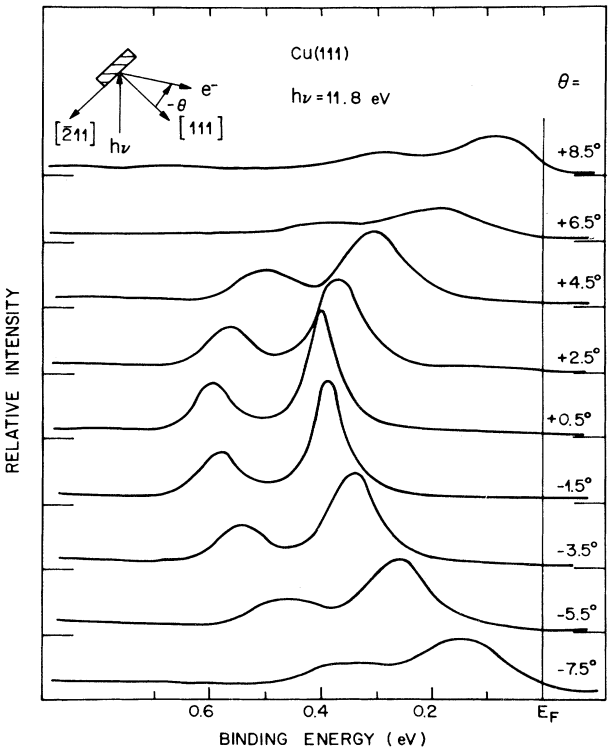

FIG. 1. Experimental EDC's for the Cu(111) *sp* surface state for several angles near normal emission in the ΓLUX plane. Second peak is due to the Ar I doublet. Energy and $k_{||}$ resolution for these data is 20 MeV and 0.018 Å^{-1} FWHM.

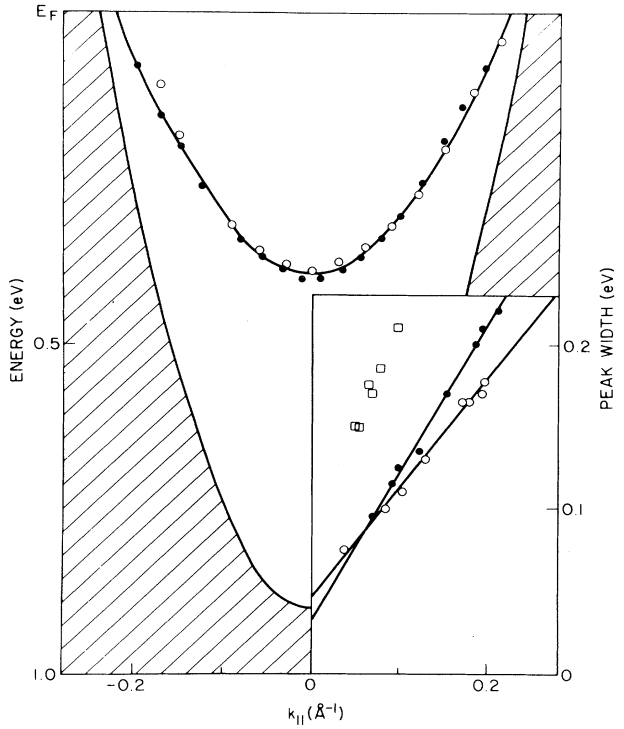

FIG. 2. Energy dispersion relation for the surface state. Solid curve is a parabolic least-squares fit. Shaded region is the projected bulk continuum of states. Inset: peak width vs $k_{||}$ for experimental momentum resolution $\Delta k_x=0.012$ Å^{-1} (open circles) and $\Delta k_x=0.025$ Å^{-1} (solid circles). Straight lines are fitted as explained in text. Also shown are data for sputtered surface with $\Delta k_x=0.025$ Å^{-1}. Energy resolution is 20 meV FWHM.

line shapes, then these four contributions would be simply additive, with the observed linewidth equal to

$$\Gamma=\Gamma_x+\Gamma_0+v(\Delta k_x+\Delta k_0)\ , \tag{1}$$

where the velocity $v=dE/dk$. For simplicity we sometimes treat the contributions as additive, when our conclusions are not affected by the modest errors thus introduced. A careful extrapolation of these and other data, to determine the intrinsic linewidth as accurately as possible, has been presented elsewhere.[6]

If we make the crude assumption that $\Gamma_t\equiv\Gamma_0+\Gamma_x$ is constant, then the data of Fig. 2 are well described by (1) with $\Delta k_0=0.029$ Å^{-1}. The fitted values of Γ_t differ only slightly despite the crudeness of taking Γ_t constant. The fits are shown as straight lines in Fig. 2. Such a reasonable fit indicates that the linewidth is dominated by Δk_0, which includes effects of *elastic* scattering, and *not* by Γ_0, which derives from decay processes. If Δk_0 is interpreted as the hole inverse mean free path, then the path length is 30 Å. Considering the concentration of impurities (typically $\approx$0.01 monolayer) and defects at even the best-prepared Cu surface, this is a very reasonable result. A more quantitative estimate of the effect of impurities is given below.

Also shown in Fig. 2 are linewidth results for a heavily sputtered Cu(111) surface. These results are not adequate to determine a good linear fit but suggest $\Delta k_0\approx0.1$ Å^{-1}, i.e., a mean free path of roughly one-third the unsputtered value. The qualitative effect of disorder on linewidth is thus as expected.

B. Cu bulk final-state lifetimes

Several experiments studying Cu bulk final-state lifetimes have been reported.[1–4] The analysis of each of these experiments employed a strict direct-transition model. Here we report results which cannot be consistently interpreted within a direct-transition model but which are well explained by relaxed $k_{||}$ conservation.

We employ an experimental configuration described by Grepstad.[1] The photon energy is fixed at $h\nu=16.85$ eV and the detector energy is chosen so that the initial state lies near E_F ($E_B=0.07$ eV). This procedure permits use of a laboratory source (fixed $h\nu$). The emission intensity $I(k_{||})$ at the detector is measured as a function of $k_{||}$ and shows a maximum at $k_{||}$ where, for some $k_\perp$, there is a direct transition of energy $h\nu$ from a state at $E_B=0.07$.

Figure 3 shows the Fermi surface of copper in the ΓLUX plane of the bulk Brillouin zone.[10] A rough estimate of the location of direct transitions at the Fermi level is obtained from the intersections labeled I and II with a free-electron final state for $h\nu=16.85$ eV. An accurate determination of the k-space location of I and II is important in the analysis which follows. We have used the triangulation technique[12,13] between the (001) and (111) surfaces and have obtained $\vec{k}_{\rm I}=(2.11,2.11,10.51)\pi/4a$ and $\vec{k}_{\rm II}=(3.67,3.67,9.36)\pi/4a$. Note that triangulating simply with the known Fermi-surface data[14] would be less accurate in some cases. A glancing intersection of a line of constant $k_{||}$ with the Fermi surface [as occurs for $\vec{k}_{\rm II}$ on Cu(100)], coupled with a small uncertainty in absolute angular calibration, can lead to large errors in determining $\vec{k}$. Triangulation between two surfaces is, therefore, crucial for high accuracy.

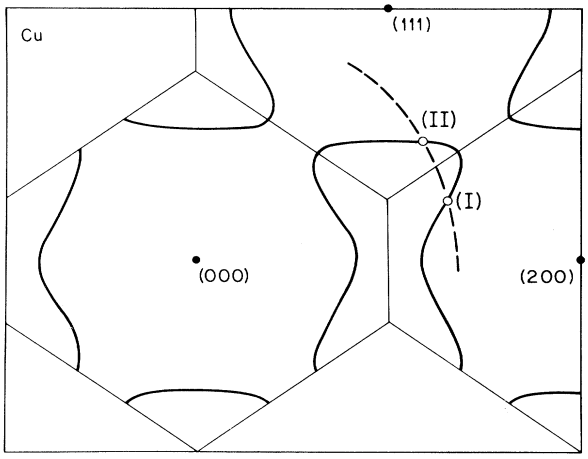

FIG. 3. Fermi surface of Cu in ΓLUX plane of bulk Brillouin zone. Free-electron surface for final-state energy of 16.85 eV intersects Fermi surface at points marked I and II. Repeated zones are shown for clarity.

For a strict direct-transition model the peak width (as a function of $k_{||}$, *not* of energy) is[1]

$$\gamma=\frac{v_{\perp e}\Gamma_h+v_{\perp h}\Gamma_e}{v_{\perp e}v_{||h}-v_{||e}v_{\perp h}}\ , \tag{2}$$

where Γ_e and Γ_h are the final-state electron and hole inverse lifetimes, and v_e and v_h are the corresponding velocities. Here the hole energy lies near E_F so its width Γ_h may be neglected, and (2) reduces to

$$\gamma=\Gamma_e/\bar{v},\quad \bar{v}\equiv v_{||e}-v_{||h}v_{\perp e}/v_{\perp h}\ . \tag{3}$$

In the following v_e has been calculated using a combined interpolation scheme[15] fitted to the stretched bands of Janak.[16] The more crucial initial-state velocities are accurately known. We estimate the errors in $\bar{v}$ introduced by this procedure to be of order 5%.

Figure 4 shows experimental plots of $I(k_{||})$ for states near II from the Cu(001) surface. These three curves were collected using the different values of experimental momentum resolution shown. A significant sharpening of the peak is observed. The natural $k_{||}$ width is determined by extrapolation to zero-momentum resolution. In extracting a width it has been necessary to subtract a smooth background from these curves—a procedure which introduces an error of 5–10%. A final systematic error arises from the fact that we must operate at a finite binding energy, so Γ_h is not exactly zero. In theory, this can be eliminated by extrapolating to $E_B=0$, but in practice we have not found such a procedure to be necessary.

Table I gives the extrapolated linewidth γ, the "effective" velocity $\bar{v}$, and the inferred electron-energy width $\Gamma_e=\bar{v}\gamma$ for each transition and each of two crystal orientations. The value of Γ_e should be independent of crystal face and is most likely also roughly the same for the two transitions (i.e., isotropic). Instead the four values are

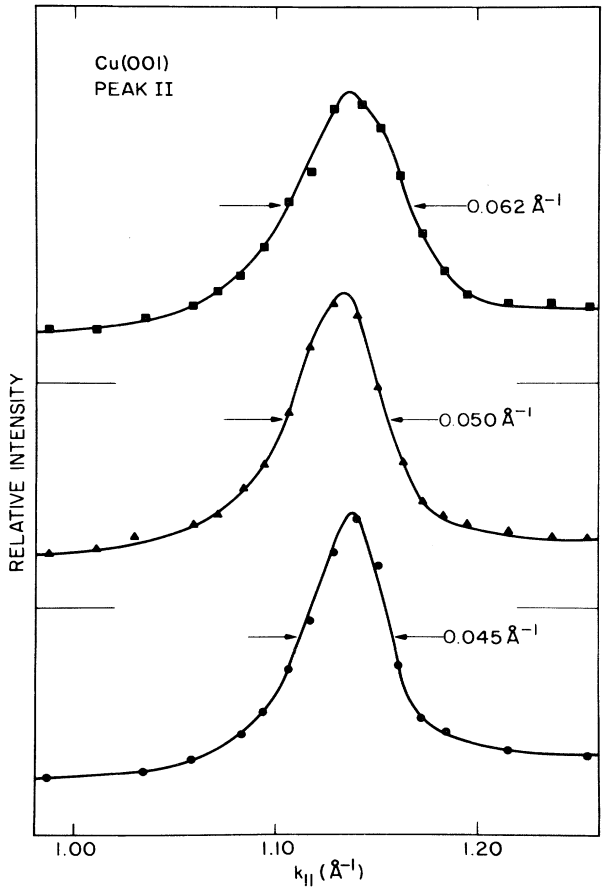

FIG. 4. Intensity $I(k_{||})$ for bulk state II on Cu(100) (cf. Fig. 3) for three values of instrumental resolution: squares, $\Delta k_x = 0.022$ Å^{-1}; triangles, $\Delta k_x = 0.014$ Å^{-1}; circles, $\Delta k_x = 0.010$ Å^{-1}. Energy resolution is 40 meV.

grossly inconsistent. We believe that these results reflect weakened conservation of $k_{||}$, as in Sec. III A.

We therefore consider the measured linewidth to consist of two contributions: a lifetime part already discussed and an additional term Δk_0 as in Sec. III A. In Table I we give the value of Δk_0 which, if subtracted from the measured linewidth γ, yields identical inferred lifetimes for the measurements of a given transition from the two different surfaces. The inferred true inverse lifetime $\Gamma_e = \bar{v}(\gamma - \Delta k_0)$ is also given.

Note that the values of Γ_e for transitions I and II are now identical to within our uncertainty, although this was not assumed. Equally important, the inferred values of Δk_0 are consistent with each other and with the value inferred from surface-state linewidths in Sec. III A. This agreement constitutes compelling evidence for the correctness of the interpretation presented.

IV. DISCUSSION

As mentioned earlier, the effects of finite mean free path are identical to those of finite angular resolution. This is evident in (1). It is therefore essential to rule out errors in the instrumental resolution Δk_x. Exhaustive tests of the apparatus are described elsewhere.[7] The variation of linewidth with angular resolution was checked in several cases and seen to obey (1). Thus, only a constant additive discrepancy between the nominal and actual values of Δk_x could account for the observed effect.

Fortunately, even this unlikely possibility can be ruled out. Recent measurements[17] of a Cu(110) surface-state dispersion for a crystal cut from a *different* (and conceivably purer) boule imply a rather smaller intrinsic broadening, $\Delta k_0 = 0.015$ Å^{-1}. We therefore conclude that the Δk_0 measured here is a property of the crystal and not of the apparatus.

Finally, it would be of great interest to identify the precise scattering mechanism at work. Unfortunately, this cannot be done quantitatively. The level of surface impurities (≈ 0.01 monolayer of sulfur and carbon) is at the limit of Auger detection and so cannot be ascertained precisely. Defect densities are even harder to quantify. It is, however, possible to calculate the mean free path (and hence Δk_0) due to impurities in the bulk. The scattering cross section is[18]

$$\sigma = 4\pi k^{-2} \sum_l (2l+1)\sin^2\delta_l \ , \tag{4}$$

where δ_l are the partial-wave Freidel phase shifts. These have been tabulated[19] for electrons at E_F in Cu, for various impurities including sulfur. The mean free path is

$$\lambda = (c\sigma)^{-1}\Omega_0 \ , \tag{5}$$

where Ω_0 is the unit-cell volume and c is the impurity concentration. For 1 at. % S in Cu, (4) and (5), along with data from Ref. 18, yield a mean free path $\lambda = 23$ Å, i.e., $\Delta k = 0.04$ Å^{-1}. Since the impurity profile at the surface is highly nonuniform, this result is only suggestive. It indicates, however, that impurity scattering from a

TABLE I. Electron lifetimes in bulk Cu. γ_k is measured linewidth (Å^{-1}), $\bar{v}\gamma_k$ is apparent inverse lifetime (eV), Δk_0 is inferred k broadening (Å^{-1}), and Γ_e is inferred true inverse lifetime (eV).

Cu	γ_k	$\bar{v}$	$\bar{v}\gamma_k$	Δk_0	Γ_e
State I, Cu(100)	0.200(10)	11.63	2.3	0.036	1.9
State I Cu(111)	0.074(5)	55.63	4.1		
State II Cu(100)	0.040(5)	283.3	11.3	0.033	1.8
State II Cu(111)	0.140(10)	17.10	2.4		

well-prepared surface is of the right magnitude to account for the observed effect. (It is worth mentioning that sulfur has an anomalously large scattering cross section since the s and p-wave shifts are close to $\pi/2$.)

An important conceptual problem obscures the effect of scattering on linewidth. LEED experiments exhibit beamwidths (Δk) limited only by the coherence length of the surface periodicity. Why should elastic scattering affect beamwidths in photoemission but not in electron diffraction?

The simplest answer is that the final-state hole in photoemission constitutes an unobserved *intermediate* state which must be summed over. The degree of energy and wave-vector conservation in the excitation process depend upon the lifetime and mean free path of the (intermediate) hole. In LEED there is no intermediate state to sum over. An alternative view is that in photoemission one deals with eigenstates of the crystal potential. These are actually scattering states, but the Fourier spectrum of a state is sharply peaked about the "ideal-crystal" wave vector corresponding to the energy of the state. In LEED one deals with eigenstates of the vacuum, which are scattered by the crystal potential.

Finally, we should point out that the conclusions drawn here concerning scattering mechanisms are tentative. Many alternatives suggest themselves. Phonon scattering can be ruled out by the absence of significant temperature dependence between 77 K and room temperature. Steps are over 200 Å apart (0.5° alignment) and so can be neglected. On the other hand, we see no easy way to clearly distinguish effects of elastic scattering of the final-state electron from scattering of the hole (i.e., of the initial electron). We attribute the observed broadening to the hole on the basis only of indirect evidence. The broadening was identical for $h\nu=11.8$ and 16.8 eV, whereas the final-state electron has quite different energy in these two cases, and so its scattering cross section should vary. Also, scattering cross sections generally decrease at higher energy, and in this case a major contaminant, sulfur, has a resonant cross section for states near E_F, favoring hole scattering. At least the order-of-magnitude difference between the mean free paths found here, and those inferred from the bulk conductivity of Cu ($\approx$400 Å even at room temperature), indicate that the mechanism for elastic scattering is specific to the surface.

As the limits of resolution in photoemission are improved, the effects described here become of significant importance. Ultimately, a systematic study of the dependence of Δk_0 on various aspects of sample preparation is needed, both to identify the sources of momentum broadening and to facilitate their elimination.

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