

Photoemission broadening of Fermi-liquid systems, and its relevance to high-temperature superconductors

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We measured at high energy and angular resolution the spectral width of photoemission features near the Fermi energy for Ag(100) and for the nearly-two-dimensional metal $2H-NbSe_2$. The results do not agree with the quadratic width-energy relationship predicted for the lifetime broadening of a Fermi liquid: We found a nearly inverse linear relationship for the sp band of Ag(100), and a similar behavior in the case of $NbSe_2$. These results indicate that the broadening is primarily affected by extrinsic factors rather than by the lifetime—and also that the “anomalous” broadening of the photoemission spectra found for the normal state of the high-temperature superconductors cannot be automatically interpreted as evidence of non-Fermi-liquid behavior.

This study concerns the causes of the photoemission spectral width for features near the Fermi energy in metals: we performed experiments with high energy and angular resolution on Ag(100) and on $2H-NbSe_2$, a nearly two-dimensional metal. The issue of the broadening dependence on the binding energy (measured from the Fermi energy) is the subject of a lively debate because of its impact on the nature of high-temperature superconductors. Several theorists have proposed that the high-temperature superconductors do not behave as Fermi liquids in their normal state; this has stimulated an intensive search for experimental evidence of deviations from the behavior of Fermi liquids.

Photoemission spectroscopy, performed with sufficient energy and angular resolution, is arguably the best way to conduct the search. Recent experiments have focused their attention on the broadening of the spectral features near the Fermi level; as it is well known, the lifetime broadening predicted for a Fermi liquid would depend quadratically on the binding energy.¹ However, Olson *et al.*^{2,3} have found for the normal state a linear dependence in the case of the $Bi_2Sr_2CaCu_2O_y$ ($BiCaSrCuO$) band that crosses the Fermi level and is involved in the opening of the superconductivity gap. This could be interpreted as evidence that this compound is not a Fermi liquid in the normal state.

Such a far-reaching conclusion, however, requires extreme prudence. There have been only a very few experiments on Fermi-liquid systems that have reached the required resolution; to our knowledge, not one of them has shown evidence of the quadratic dependence predicted for Fermi-liquid lifetime broadening.^{1,4} This stimulated us to use our high-resolution apparatus and explore this crucial problem.

Our study addresses two specific issues. Previous experiments with high resolution by Kevan *et al.*⁵ have discovered cases of nonquadratic dependence for surface-state bands of different metals; in fact, the rela-

tion is even qualitatively different from the Fermi-level lifetime broadening, since the bandwidth decreases as the binding energy increases—indicating that lifetime is not the primary factor in the observed linewidth. Is this, however, a result that can be generalized to bulk states? We explored this first issue by studying the broadening of bulk states in Ag(100), finding a qualitative width-energy relation similar to that of the surface bands although the magnitude of the widths is much larger. Further, is the width-energy relationship found for $BiCaSrCuO$ peculiar to the nearly two-dimensional character of this crystal? We explored the issue by performing broadening measurements in a layered, nearly two-dimensional compound that is not a high-temperature superconductor: $2H-NbSe_2$. We found again a qualitative width-energy relation similar to that found for three-dimensional metals. Our experiments were completed by careful studies of broadening for $BiCaSrCuO$ and for several surface-state bands of silver, that gave results consistent with those of other investigators, enabling us to link the present data with theirs.

We conclude, as discussed below in detail, that, to date, no evidence of a system exists in which the photoemission spectral width behaves as predicted for Fermi-liquid lifetime broadening, and that the “anomalous” broadening found for $BiCaSrCuO$ cannot be used as conclusive evidence for a non-Fermi-liquid nature of this material in its normal state.

The photoemission experiments were performed with 4-m normal-incidence monochromator and with a Seya-Namioka monochromator at the Wisconsin Synchrotron Radiation Center. The photoelectrons were analyzed in energy and angle with a Vacuum Science Workshop hemispherical analyzer. The samples were kept under ultrahigh vacuum, and their temperature was controlled with a resistive heater and with a closed-cycle He refrigerator.

The combination of the high photon flux, high photon

energy resolution provided by the beamline, and the high-energy resolution of the electron analyzer when operated at low-pass energies, enabled us to reach a high overall energy resolution, without need for large acceptance angles. The best performance of the system is an energy resolution (Gaussian equivalent, full width at half maximum) of 15 meV, with an angular resolution of $\pm 1^\circ$.⁶ The routine performance in the present study is 20–30 meV.

Clean Ag(100) surfaces were prepared with standard *in situ* sputter-anneal processing. The NbSe₂ single crystals were simply cleaved *in situ*. During the experiments, there was no observable contamination, such as chemisorption or noble-gas physisorption on the surfaces.

In the first series of experiments, we studied the near-Fermi-edge *sp*-like state of Ag(100), along the $\bar{\Gamma}-\bar{X}$ direction in **k** space. Photoemission spectra were taken with five different photon energies in the 12–30 eV range, both at room temperature and at 70 K. Figure 1 illustrates the position in energy of this peak as a function of the **k** vector (the procedure to determine the peak position is discussed below). The solid line is a second-degree-polynomial fitting. The observed dispersion in this figure agrees with previous experimental studies.⁷

Figure 2 shows a set of angle-resolved photoemission spectra, illustrating the behavior of the peak as it approaches the Fermi energy. From these spectra, the deviations from Fermi-liquid lifetime broadening are evident: The width of the peak is quite large, and not only does it not decrease as the peak approaches the Fermi level, but it actually increases. This is precisely the qualitative width-energy relation that had been reported for surface-state peaks,⁵ only in this case the band corresponds to a bulk state.

In order to accurately determine where in **k** space the band crosses the Fermi surface, we show in Fig. 3 the photoemission intensity as a function of the polar angle. Considering again Fig 2, we can appreciate that the spectral width of the peak never decreases as it approaches the Fermi energy, not even when its centroid is only a few millivolts below this energy. This is further confirmation of the “anomalous” energy dependence of the spectral broadening.

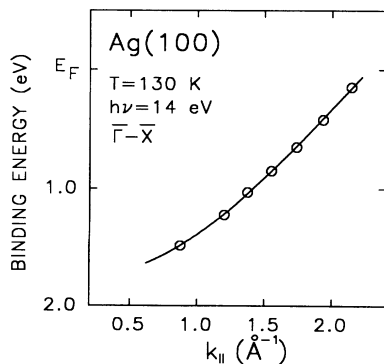


FIG. 1. Experimentally determined dispersion of the near-Fermi-edge bulk band of Ag(100).

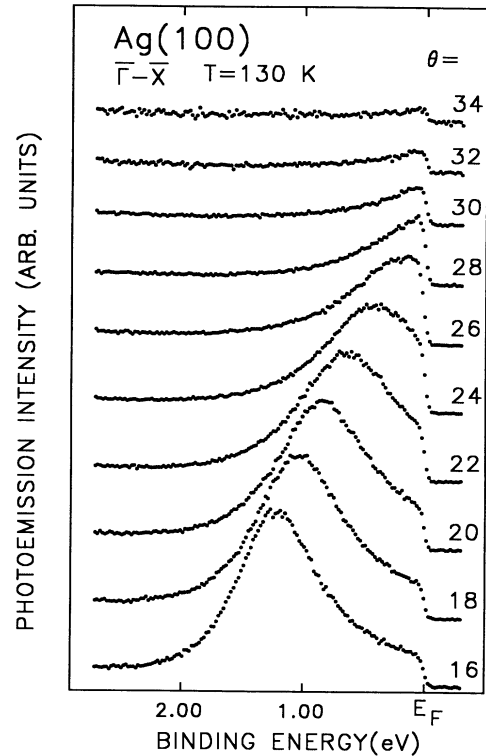


FIG. 2. Photoemission spectra showing the dispersing band of Fig. 1, as it approaches and crosses the Fermi energy.

We analyzed the data to estimate the functional dependence of the linewidth on the binding energy. The line shape of the near-Fermi-energy peak was approximated by a Voigt function multiplied by the Fermi-Dirac function; the parameters of the Voigt function were determined by least-squares fitting; this enabled us, in particular, to estimate the peak position in energy and its Lorentzian-equivalent full width at half maximum (FWHM).

Typical results of this fitting procedure are shown in Fig. 4. We can see that the quality of the fit is very high

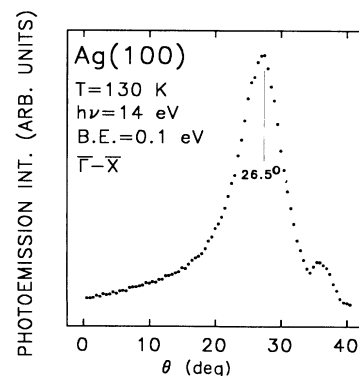


FIG. 3. Photoemission intensity at a binding energy 0.1 eV below the Fermi level, as a function of the polar angle. The figure can be used to monitor the band as it crosses the Fermi energy at a polar angle of approximately 26.5°.

when the peak is near the Fermi energy. As the distance from the Fermi energy increases, we see that the peak appears increasingly asymmetric, a feature that cannot be reproduced by a Voigt-function fitting. The cause of the asymmetry is the finite angular acceptance. We tested *a posteriori* the reliability of the parameters estimated from our fitting procedure by simulating the effects of the angular acceptance on the corresponding line shape and checking that the resulting distorted line shape reproduces the asymmetric experimental line shape. The results of these tests were positive for all of the data discussed in this article.

Figure 5 shows the Ag-*sp*-band peak FWHM as a function of the binding energy, both parameters being again determined from the fitting procedure. Two sets of data

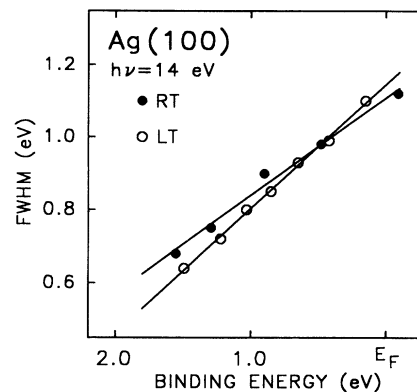


FIG. 5. Full-width at half maximum (Lorentzian equivalent of the Voigt function) as a function of the binding energy (measured from the Fermi level) for Ag(100) at two different temperatures. The binding energy (BE) is shown, as well as the analyzer's pass energy (PE)

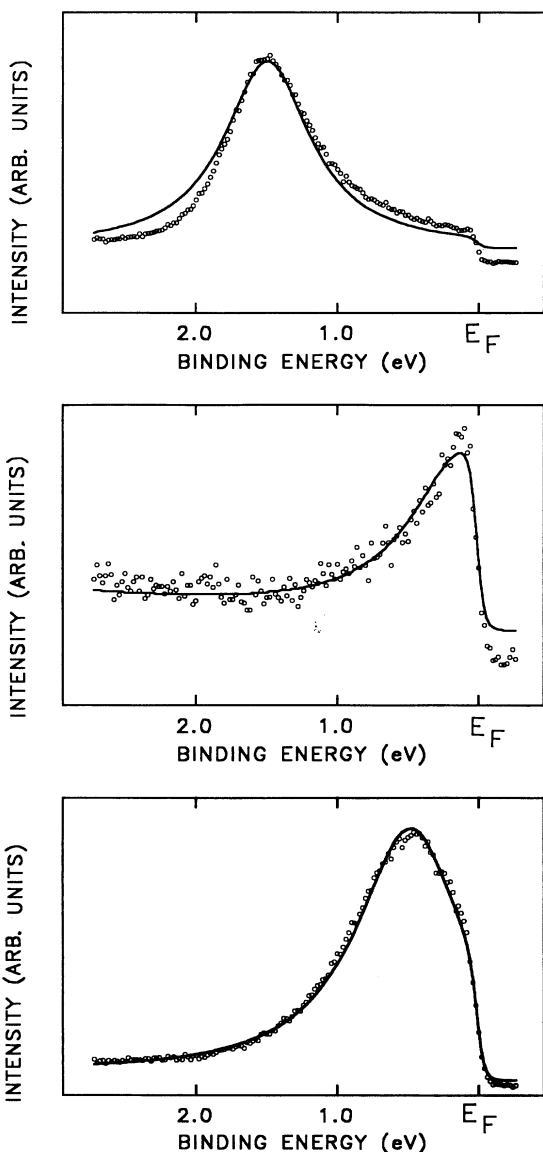


FIG. 4. Results of the line shape fitting described in the text, for three different spectra corresponding to peaks at different distances from the Fermi energy.

are shown for two different temperatures. We clearly see that the peak width is quite large, and that a quadratic increase of the FWHM, with the distance from the Fermi energy, is qualitatively inconsistent with the data. We see instead a decrease, approximately linear with the distance from the Fermi energy. The slope of this linear relation does not change much with the temperature.

Furthermore, the absolute value of the FWHM is only slightly affected by the change in temperature. The temperature dependence of the FWHM is explored in Fig. 6, which illustrates the width as a function of temperature for a specific set of experimental conditions corresponding to a peak binding energy of -450 meV. We do see a

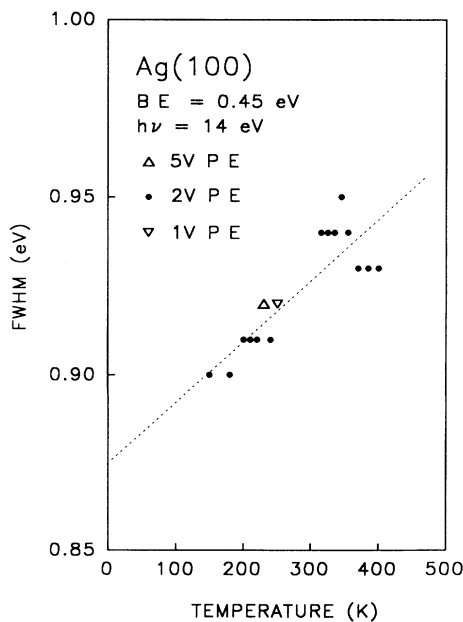


FIG. 6. Full-width at half maximum of Ag(100) as a function of the temperature.

limited but observable dependence on the temperature (not detectably affected by changes in the analyzer's pass energy, i.e., in the instrumental broadening). Note that the total change with temperature in the range 130–400 K is only approximately 50 meV, whereas the total FWHM is of the order of 1 eV. The temperature dependence can be approximated by a linear relation (dashed line in Fig. 6); extrapolating this linear relation, a width of approximately 0.8 eV can be obtained as the intrinsic linewidth at absolute zero, a magnitude still much larger than that of the temperature variations in Fig. 6.

Other series of spectra were taken with different photon energies, ranging from 12 to 40 eV. From these data, we derived width-energy relations that coincide with those of Fig. 5. The relation, therefore, does not depend on the photon energy. This indicates that the broadening is not affected by the possible occurrence of indirect transitions.

The second issue addressed by our work, i.e., that of the width-energy relation for a nearly two-dimensional crystal, was explored using NbSe_2 data like those of Figs. 7 and 8. Figure 7 shows a series of spectra revealing a downwards-dispersing peak near the Fermi edge as we move away from the center of the Brillouin zone. The limited dispersion observed here is consistent with the theoretical predictions for the $d_{x^2-y^2}$ band in this material, as well as with previous experimental band-mapping studies.^{8,9} The weak dispersion makes it more difficult to appreciate the width-energy relation in Fig. 7 for silver than from mere visual inspection.

Note, however, that by comparing the upper curves in Fig. 7 it is possible to observe that the width once again decreases rather than increasing as the distance from the Fermi energy increases; this is another example of

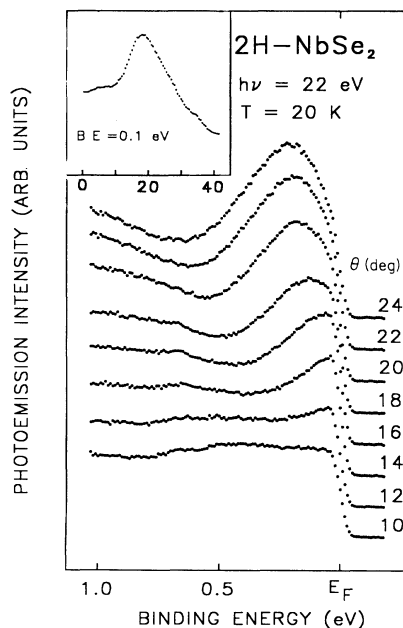


FIG. 7. Photoemission spectra of a weakly dispersing band of niobium diselenide. The inset is a plot equivalent to that of Fig. 3 in the case of Ag.

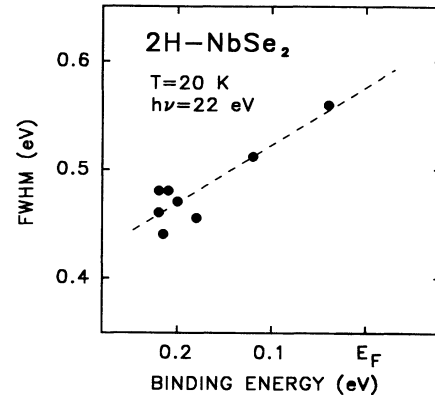


FIG. 8. Full-width at half maximum of the niobium diselenide band near the Fermi energy, as a function of the binding energy.

dramatic discrepancy with respect to the predictions of Fermi-liquid lifetime broadening. The width-energy relation was more accurately derived using the same fitting procedure as for the silver data, and the results are shown in Fig. 8. As in the case of silver, we certainly do not see a narrow width quadratically increasing with the distance from the Fermi energy, but rather an approximately linear decrease of a rather large FWHM.

As an aside, we observed in Fig. 7 evidence that the band disperses and crosses the Fermi energy. This behavior was not reported by previous studies of the same material.⁸ This apparent discrepancy could originate from the improvement in resolution with respect to the previous experiments.

Note that $2H\text{-NbSe}_2$ exhibits a phase transition with the onset of a charge density wave. We performed experiments at temperatures above and below the transition point, demonstrating that our conclusions on the width-energy relation are not affected by the phase transition. Another potential complication is the possible presence of two different weakly dispersing bands in this energy region. Even if this was the case, however, we could still rule out a sharpening of the peak as it approaches the Fermi energy; therefore, our main conclusion against a Fermi-liquid lifetime broadening stands. Finally, temperature effects were again very small and therefore could not account for the observed width-energy relation.

The main purpose of this work is to demonstrate that ordinary two- and three-dimensional metals do not exhibit the photoemission spectral width predicted for Fermi-liquid lifetime broadening. We prefer, therefore, to refrain from a full analysis of the possible causes of broadening. We would like to mention, however, that several possible explanations of this "abnormal" broadening (for the case of metal surface states) have been proposed by Kevan *et al.*⁵ They included broadening due to surface imperfections, phonon scattering, finite energy, and angular resolution. We do not believe, however, that any one of these factors can fully explain our data.

As to surface imperfections, our surfaces exhibited good ordering and excellent cleanliness as tested with low-energy electron diffraction and photoemission stud-

ies. Also consider that in the case of silver the FWHM for states 100 meV from the Fermi level is approximately 400 meV; such a broadening would require an electron scattering length from impurities of only a few angstrom, i.e., scattering from almost every surface atom, which is physically unreasonable.

Finite energy resolution does not appear as an important factor in our present studies because it is much better than the peak FWHM; it was, in fact sufficient to study the behavior of much narrower peaks such as the surface bands of silver or the superconducting state near-Fermi-edge feature of BiCaSrCuO. We have already discussed the effects of finite angular acceptance, and we have seen that they are essentially confined to causing a slight asymmetry of the peaks; they certainly cannot account for a qualitative change in the width-energy relation. This conclusion is strengthened by the data on $2H\text{-NbSe}_2$: since the dispersion is much less than for silver, the finite angular resolution would have even less impact on the broadening, yet our qualitative observations on the width-energy relation are equivalent for the two materials. Because of the line shape asymmetry, however, we cannot rule out other effects due to finite momentum resolution, such as those related to surface roughness; such effects could be particularly important for Ag, as suggested by roughness-enhanced Raman experiments that reveal a high density of surface defects. Finally, our temperature-dependent studies indicate that phonon broadening is a minor factor for these large widths, and unlikely to explain by itself the “anomalous” broadening that we observed.

In conclusion, our study addressed several issues concerning the broadening of near-Fermi-edge photoemis-

sion peaks in three- and two-dimensional metals. We found peak widths that decreased with the distance from the Fermi energy rather than increasing, such a decrease being approximately linear. This result is qualitatively similar to that previously obtained⁵ for the surface bands of several metals, and we have therefore demonstrated that it is not peculiar to those bands. Specifically, we have demonstrated that the decrease in FWHM with the distance from the Fermi energy is not confined to surface bands, because we observed it for bulk bands as well as for surface bands; it is not confined to three-dimensional metals because we observed it for a nearly two-dimensional metal.

The width-energy relation and the magnitude of the width are in clear disagreement with the predictions of a Fermi-liquid lifetime broadening. This suggests that extreme prudence be exercised the interpretation of the “anomalous” width-energy relation for BiCaSrCuO. Before attributing it to deviations from Fermi-liquid behavior, it is important to clarify the causes of broadening in systems such as those explored here, that are good examples of Fermi liquids but do not exhibit the lifetime broadening of a Fermi liquid.

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