High-resolution tests of low-dimensionality effects in photoemission

C. Coluzza, H. Berger, P. Alméras, F. Gozzo, and G. Margaritondo
Institut de Physique Appliquée, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

G. Indlekofer
Institut für Physik, Universität Basel, CH-4056 Basel, Switzerland

L. Forro
Institut de Génie Atomique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Y. Hwu
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
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High-energy-resolution photoemission spectra, taken on three quasi-one-dimensional crystals, $TaTe_4$, $NbTe_4$, and $(NbSe_4)_3I$ confirm the general phenomenon of the suppression of the photoemission intensity near the Fermi level in one dimension. We analyze the possible causes of this phenomenon in light of previous results on $(TaSe_4)_2I$.

I. INTRODUCTION

A series of exciting results have recently stimulated much interest in the role of dimensionality in solid-state photoemission.[1-3] We have investigated these effects in $TaTe_4$, $NbTe_4$, and $(NbSe_4)_3I$—three crystals with strong one-dimensional character—exploiting the advanced performances of the undulator synchrotron beamline at the LURE Laboratory. The high-energy resolution made possible by this beamline enabled us to confirm an apparently general effect of one dimensionality: the suppression of the photoemission signal near the Fermi level.[1-3] Combined with previous studies[2] of $(TaSe_4)_2I$, these results rule out all of the explanations that have been so far proposed for this phenomenon, except correlation effects.[4] Thus, the suppression is either due to correlation or to a still unknown mechanism.

The interest in low-dimensionality effects in photoemission initiated in the case of nearly two-dimensional materials and, specifically, the high-temperature superconductors.[5] Early results on low-quality YBCO specimens exhibited a low signal level near the Fermi edge, and this stimulated speculations about correlation being the cause of this suppression. Subsequently, the discovery[6] of a clear Fermi edge in the spectra of BCSCO and careful studies of YBCO and other high-temperature superconductors identified oxygen stoichiometry problems as the real cause of the suppression.

Recently, Dardel *et al.*[2] presented the first high-energy-resolution angle-integrated photoemission study of a nearly one-dimensional material, $(TeSe_4)_2I$, observing a marked decrease in the photoemission intensity for the region within ≈ 0.5 eV of the Fermi level E_F. Similar phenomena had been suggested by previous studies performed at lower resolution,[1] and it was suggested that they are a general characteristic of one-dimensional systems. Several mechanisms were discussed by Dardel *et al.*[2] as possible causes of the effects, including a real lack of states near the Fermi level, fluctuations,[7] phonon-assisted processes,[8] and correlation.[4]

Angle-resolved photoemission data on the same compound,[3] combined with temperature-dependent studies and other data,[2] ruled out most of these mechanisms. In particular, a low density of states near E_F would not agree with the observed Peierls transitions in $(TaSe_4)_2I$, and in other nearly one-dimensional materials.[7] Phonon-assisted processes would require an unrealistically high number of phonons to justify the intensity shift from the edge region; furthermore, no evidence for such processes is found for other spectral features. Fluctuation effects would produce a temperature dependence of the spectra that is not observed.[2] Correlation effects, therefore, are the only surviving explanation of those proposed so far for the near-edge suppression of the photoemission signal. But one cannot exclude other, yet unknown mechanisms.

One point was not clear from the earlier experiments on $(TaSe_4)_2I$: is this phenomenon a general property of one dimensionality? In order to clarify this critical issue, we initiated a systematic investigation of the photoemission spectrum of nearly one-dimensional crystals. The results for the first three compounds in this class, presented in this paper, confirm that the effect occurs for materials other than $(TaSe_4)_2I$, and therefore support the hypothesis that the suppression of the photoemission signal near the Fermi edge is indeed a general one-dimensional phenomenon.

Note that the low intensity near the Fermi edge cannot be an artifact of the photoemission process, since many other types of materials—notably simple and transition-metal samples—exhibit under similar conditions a clear signal at the Fermi edge: the phenomenon appears then related to the peculiar properties of this quasi-one-dimensional family of crystals. Also note that photoemission probes a near-surface region whose thickness is of the order of tens of angstroms. We cannot exclude that

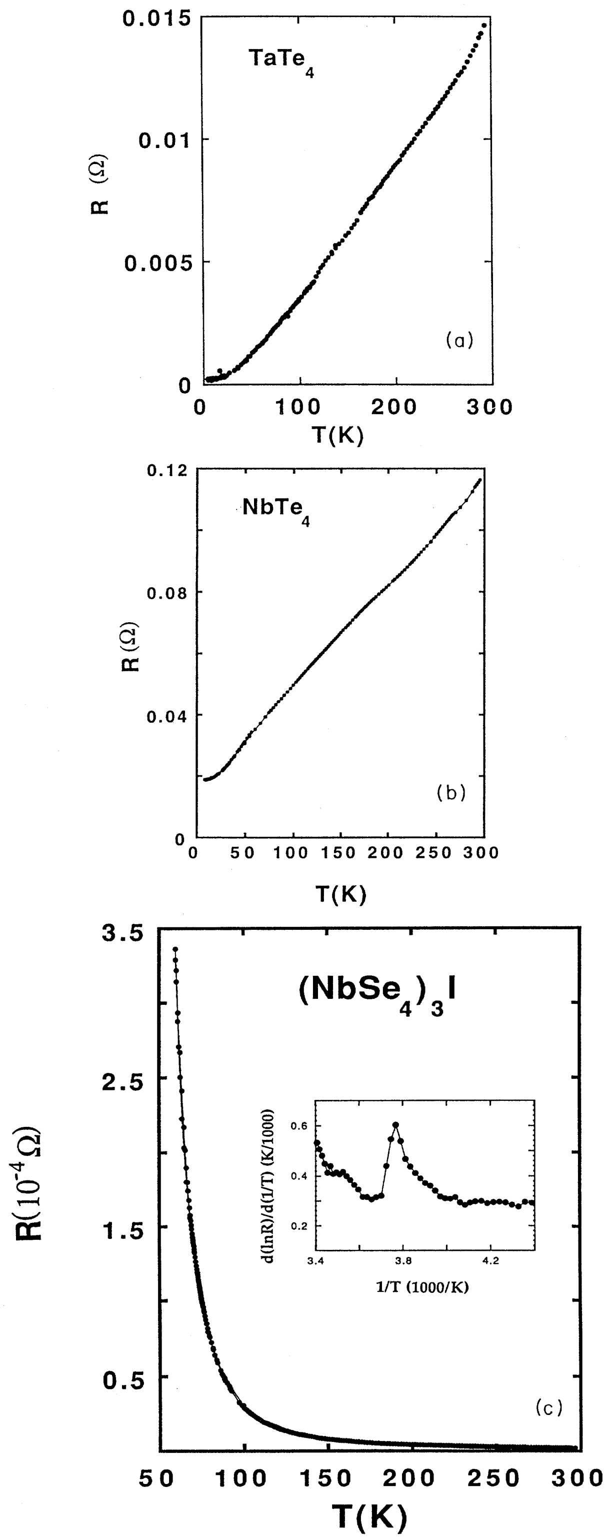

FIG. 1. Resistance vs temperature measurements for the three nearly one-dimensional materials investigated by our experiments: (a) $TaTe_4$, (b) $NbTe_4$, and (c) $(NbSe_4)_3I$. The results reveal the metallic character of the first two materials, whereas the third behaves as a semiconductor. The inset in (c) shows a derivative plot and emphasizes the phase transition of $(NbSe_4)_3I$.

the observed suppression is a surface-related phenomenon. We note, however, that the phenomenon must still be peculiar to the characteristics of this family of compounds, since surface sensitivity is not sufficient to suppress the photoemission edge intensity for other materials.

II. EXPERIMENTAL PROCEDURE

Single-crystal $TaTe_4$, $NbTe_4$, and $(NbSe_4)_3$ were grown at the Institut de Physique Appliquée of the Ecole Polytechnique Fédérale de Lausanne, using the vapor transport method described in Ref. 9. For $TaTe_4$ and $NbTe_4$, the transport agent was tellurium chloride, whereas for $(NbSe_4)_3I$, it was iodine. The procedure produced high-quality single crystals, in the shape of plates as large as 1 cm^2, with a needlelike substructure. The crystals were characterized with x-ray crystallographic tests and transport measurements.

Resistivity versus temperature measurements (see Fig. 1) revealed a markedly metallic behavior for $TaTe_4$ and $NbTe_4$, and a semiconducting behavior for $(NbSe_4)_3I$. The nearly one-dimensional character of the crystal structure is quite evident in Fig. 2, and shows a series of weakly interacting chains. The structure is similar for $TaTe_4$ and $NbTe_4$, whereas for $(NbSe_4)_3I$ the iodine atoms are situated between chains, further enhancing the one-dimensional character.

$NbTe_4$ exhibits[10] a charge-density wave (CDW) at room temperature with an incommensurate structure; it also exhibits an incommensurate-incommensurate phase transition at 180 K, and the structure becomes commensurate at 50 K. For $TaTe_4$, a commensurate-commensurate transition occurs only at 450 K, above room temperature. $(NbSe_4)_3I$ exhibits a non-CDW phase transition at 275 K, primarily revealed by transport measurements. The inset in Fig. 1(c) emphasizes this latter

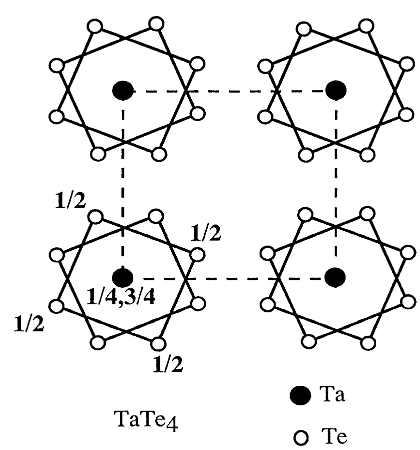

FIG. 2. The chainlike structure of $TaTe_4$ (and $NbTe_4$) is evident from its projection on a plane perpendicular to the chains (Ref. 11). The structure of $(NbSe_4)_3I$ is related to that of $TaTe_4$, but the iodine atoms are situated between chains, increasing the interchain distances and further enhancing the one-dimensional character.

phase transition.

The samples were cleaved or scraped under a ultrahigh vacuum in the photoemission system connected to the Swiss-French LURE (SU3) beamline. We note that samples in this family have stable surfaces, similar to those of most layer compounds such as the III-VI's. They do not, in particular, exhibit the stoichiometry problems that affected most of the early work on high-temperature superconductors, mainly related to the loss of oxygen. The high quality of our present surfaces is an absolute requirement, for example, for the observation of sharp dispersing features in angle-resolved photoemission (also Ref. 3). The photon source of the beamline is an undulator installed on the SUPERACO storage ring, whose emission is further monochromatized by a Jobin-Yvon plane-grating monochromator. The spectral range of the beamline is 10–300 eV.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Photoemission experiments are performed with a Vacuum Science Workshop hemispherical electron analyzer. The combination of the high-brightness source, of the monochromator, and of the high-performance analyzer makes it possible to obtain high-energy resolution and a high signal level, as required for the present experiments. Preliminary tests of the SU3 line have achieved energy resolutions for solid-state photoemission in the 10-meV range (and angular resolutions of 0.5°).

In the present experiments, the typical Gaussian energy resolution at room temperature was 40 meV. The spectra were taken with a large-angle collection geometry, roughly corresponding to the first two Brillouin zones in k space, to achieve reasonable averaging in the direction parallel to the chains. This point was corroborated by comparing data taken on cleaved and scraped samples, since the scraping increases the angular averaging. Furthermore, we took spectra for a series of collection cones centered at different directions normal to the chains, to rule out spurious angular effects in the observed intensity suppression near the Fermi level. All of these tests support our conclusions on the properties and nature of this phenomenon.

The main issue explored by our experiments is the intensity of the signal near the Fermi level. Figure 3, which shows room-temperature photoemission spectra for the three crystals, already suggests an anomalously small signal for the two binary compounds, considering their clearly metallic nature.

In order to confirm this suppression of photoemission intensity, we took high-energy-resolution spectra near E_F at several different temperatures, in the range from room temperature (RT) to liquid nitrogen. Figures 4 and 5 show a series of such high-resolution spectra, taken at RT and 100 K, at a photon energy of 24.2 eV. A spectrum taken at RT on scraped molybdenum is shown for comparison.

The low intensity of the photoemission signal near the Fermi energy is again clear for the quasi-one-dimensional samples. Notice, however, that in all three materials we do observe some signal all the way up to the Fermi level,

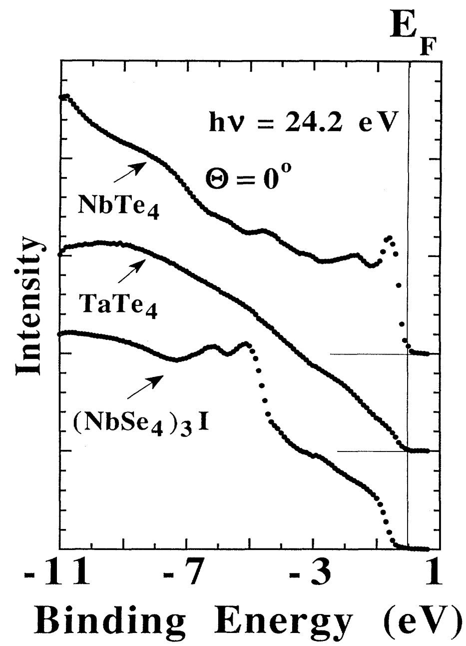

FIG. 3. Photoemission spectra taken on the three compounds with a photon energy of 24.2 eV. The samples were kept at room temperature; in this case, the $TaTe_4$ sample was cleaned by scraping whereas the other two were cleaved. The angle Θ refers to the central direction of the photoelectron collection cone, and $\Theta=0$ means a direction perpendicular to the chains. Note, however, that the angular integration essentially covered the entire reduced zone along the chains.

whereas for $(TaSe_4)_2I$ the photoemission intensity near E_F is vanishing.[2,3] The $TaTe_4$ and $NbTe_4$ spectra of Figs. 4 and 5 actually suggest a suppression of the photoemission signal with respect to the level that one could expect from the density of states at the Fermi edge in a one-electron picture. In the case of $(NbSe_4)_3I$, a weak but measurable signal is also present up to the Fermi level, in spite of the semiconducting transport properties of this compound.

How can the absence of signal near the Fermi energy be explained for the metallic compounds? First of all, we note that there is additional good evidence, besides the metallic character, against the hypothesis of an intrinsically low density of states near E_F. In fact, all materials exhibit phase transitions that require a sufficiently high density of states near the Fermi level.[10]

The theoretical band structure[11] of $NbTe_4$ is also in conflict with the hypothesis of an intrinsically low density of states near the Fermi edge, since it predicts a band that crosses the Fermi edge in the outer part of the reduced zone, along the chains. Such a band was not observed[3] in the angle-resolved spectra of $(TaSe_4)_2I$, and the corresponding contributions to the density of states are consistently absent from our spectra. We also analyzed the possibility that the density of states follows a true one-dimensional behavior (inverse square root) with a decrease as the energy increases. However, model calculations with the parameters of $TaTe_4$ cannot justify the rap-

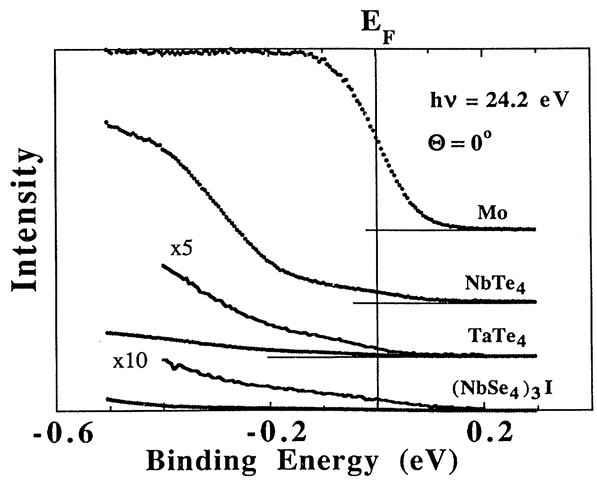

FIG. 4. High-energy-resolution photoemission spectra taken on the three compounds at room temperature and on a scraped molybdenum sample (for comparison). In this case, the $TaTe_4$ sample was cleaved as the other two one-dimensional compounds.

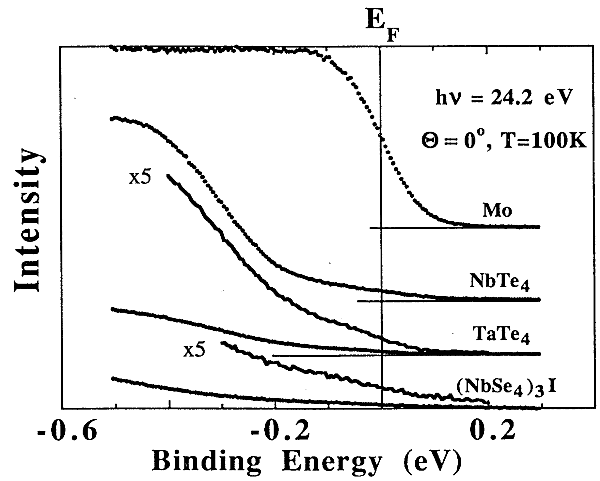

FIG. 5. High-energy-resolution spectra of our quasi-one-dimensional compounds, taken in conditions similar to those of Fig. 4 except for the temperature ($T = 100$ K). A molybdenum spectrum is again shown for comparison.

id signal decrease seen in Figs. 4 and 5 as the energy approaches E_F: they predict, instead, a nearly flat energy dependence in this narrow spectral region.

As to the other effects proposed so far,[2] to explain the low signal near the Fermi edge we already mentioned that for $(TaSe_4)_2I$, angular-integrated and angular-resolved data[2,3] ruled out all of them except correlation.[4] We believe that the same conclusion can be extended to the present data, at least in the case of $TaTe_4$ and $NbTe_4$. First, consider possible fluctuation effects. The strongest argument against them in the case of $(TaSe_4)_2I$ was the absence of the predicted temperature dependence of the spectra.[2,3] Also, the measured pseudogap[7] was much smaller than the width of the spectral region affected by the suppression of the photoemission signal. In the present case, there are again no noticeable temperature effects. Furthermore, for $TaTe_4$, there is no evidence of a pseudogap in the explored temperature range, yet the photoemission signal is still weak near the Fermi energy.

The hypothesis of a phonon-assisted photoemission mechanism with a decrease of the photoelectron energy[2,8] was also ruled out for $(TaSe_4)_2I$, primarily on the basis of the spectral feature line shape and because the angle-resolved spectra did show a dispersing feature with no evidence of phonon satellites.[3] In the present case, we cannot use directly the same argument. We note, however, that the shallowest peak observed in Fig. 3 for $NbTe_4$ is quite consistent with a flat-band region of the calculated band structure (see Ref. 11), primarily due to nondispersion along the directions perpendicular to the chains. The energy of this feature appears too close to the theoretical expectations to be consistent with phonon-assisted processes producing large energy shifts. A related (although weaker) feature is visible at similar energies for the other two compounds.

In summary, we used the high resolution of the new SU3 beamline at LURE to test the hypothesis that one dimensionality implies low-photoemission intensity near the Fermi energy. We found for all studied compounds a behavior similar to that previously reported for $(TaSe_4)_2I$: the signal is very weak, even in the case of samples with clear metallic character. Our data, therefore, support the hypothesis of a generalized one-dimensional effect.

As to the causes of the effect, we can rule out all proposed mechanisms except for correlation effects,[4] although we do not have positive evidence proving them, and we cannot, of course, rule out other, still unknown phenomena. Further experiments are underway to seek evidence in favor of correlation effects or against them, and also to check several critical issues concerning these low-dimensionality effects. We note that the result could have a significant impact on other low-dimensionality systems, and specifically on high-temperature superconductors, many of whose photoemission features remains unexplained in spite of very extensive studies.

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