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Electronic structure and the metal-insulator transition in $\mathrm{NiS}_{2-x}\mathrm{Se}_x$

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We studied the metal-insulator transition in the $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ system in $x=0$ and $x=0.5$ single crystals using angle-resolved photoemission. A narrow band, characteristic of many-body effects, develops near E_F for $x=0.5$. This feature shifts away from E_F at the transition temperature, a discontinuous change at the metal-insulator transition in a Mott-Hubbard system. We discuss our data in the context of recent theoretical calculations of the Hubbard model. The spectra support the general finding that a narrow peak of many-body nature develops at E_F during the insulator-to-metal transition.

The discovery of copper oxide based high-T_c superconductors and their related metal-insulator transition (MIT) problem has renewed interest in MIT's in transition-metal compounds. Aside from the high-T_c compounds, MIT's have been studied in the transition-metal compounds $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ (Ref. 1) and $(\mathrm{V}_{1-x}\mathrm{Ti}_x)_2\mathrm{O}_3$ (Ref. 2) by means of transport measurements. $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ is a good system in which to study the MIT because the transition is not believed to be complicated by a change in structural symmetry, as suggested by x-ray diffraction[3] and Raman-scattering experiments.[4,5] In the $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ system, NiS_2 is an insulator; the system shows an MIT at $x<0.45$ for $T=0$ K. $\mathrm{NiS}_{1.5}\mathrm{Se}_{0.5}$ is an insulator at high temperature and a metal at low temperature, exhibiting an MIT at ~60 K.[6]

In this paper, we report results of angle-resolved photoemission spectroscopy (ARPES) studies of $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ for $x=0$ and $x=0.5$ single crystals. We observe a narrow band near the Fermi energy in the metallic $x=0.5$ crystals, which is absent in the insulating $x=0$ crystals. The appearance of this narrow band with Se substitution cannot be explained by band theory. Experimental data and electronic structure calculations suggest that the MIT can be explained qualitatively by an effective one-band Hubbard model. This analysis leads to the intriguing possibility that the narrow band in our data is related to the sharp peak in the spectral weight function on the metallic side of the MIT predicted by infinite-dimensional Hubbard model calculations. We also present temperature dependence data from the $x=0.5$ crystal, in which we observe an abrupt energy shift in the near-E_F spectral feature at the MIT temperature.

We performed ARPES experiments at undulator beamline 5 at the Stanford Synchrotron Radiation Laboratory. For 22.4-eV and 38-eV photon energies, the energy resolution of our data is ~35 and ~85 meV, respectively. The samples were single crystals of $\mathrm{NiS}_{2-x}\mathrm{Se}_x$, grown by the chemical vapor transport method using bromine as a transport agent,[7] as in previous works.[8] The crystals had shiny (100) and (111) facets and had linear dimensions of 1–2 mm. The samples were cleaved, along their natural (100) cleavage planes, in a UHV chamber operating at a base pressure of 6×10^{-11} Torr.

Figure 1 shows a comparison of ARPES spectra in both the insulating $x=0$ material and in the metallic temperature regime of the $x=0.5$ material. We observe clear dispersion in the spectra, indicating that our samples are good single crystals. The dispersive behavior of the most prominent valence-band feature (marked by arrows) is similar in the $x=0$ and the $x=0.5$ samples. The most obvious difference between the results from the NiS_2 crystal and the $\mathrm{NiS}_{1.5}\mathrm{Se}_{0.5}$ crystal is that in the $x=0.5$ sample a narrow band appears near the Fermi energy. The narrow band exhibits minimal dispersion, although its intensity changes with emission angle. This band is not present in the $x=0$ case. The narrow-band peak is much stronger in intensity at higher photon energies, as illustrated by comparing the uppermost spectrum in Fig. 1(b), taken at 38 eV, with the rest of the spectra, taken at 22.4 eV. The peak is absent in the $x=0$ samples for higher photon energies, as shown in the uppermost spectrum of Fig. 1(a).

As we will discuss later, the narrow band is a manifestation of the MIT and cannot be explained by local-density approximation (LDA) calculations. The main valence-band features are hybrid Ni 3d and S/Se p states with predominantly p character so that NiS_2 is a charge-transfer insulator. It is difficult to compare the dispersion of these features to the theoretical calculations, since our angle-resolved photoemission spectroscopy data from these three-dimensional crystals are not taken along a high-symmetry direction. Since we are mainly interested in the MIT of this system, we will limit our discussion to only the near-E_F feature.

We studied the temperature dependence of the near-E_F band of the $x=0.5$ crystal at photon energies of 38 eV, where the near-E_F feature exhibits strong intensity, and at 22.4 eV, where we obtain our best energy resolution. Spectra were taken starting from low temperatures and progressing to higher temperatures. After each experiment, the sample was cooled down to confirm reproducibility of the low-temperature spectra. Figure 2 shows 22.4-eV spectra, where we obtain our best energy resolution and see a very small

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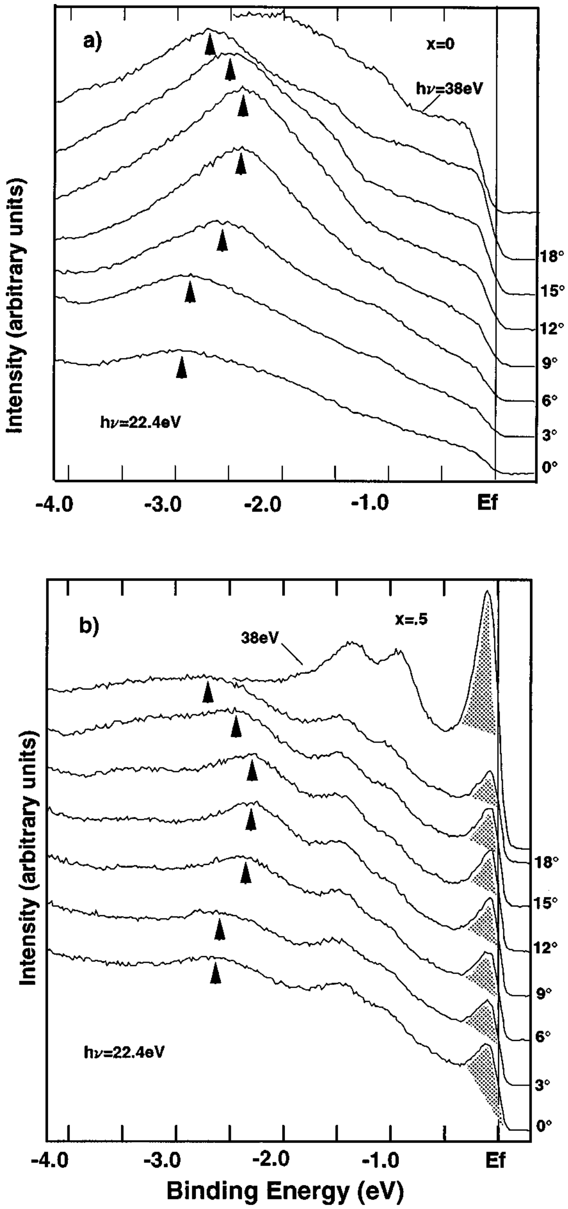

FIG. 1. Valence-band spectra spanning approximately one Brillouin zone. The top panel is the $x=0$ sample at $T=30$ K. The bottom panel is the $x=0.5$ sample at $T=45$ K, in the metallic regime. The spectra labels indicate the analyzer angle. We have shaded the near-E_F feature.

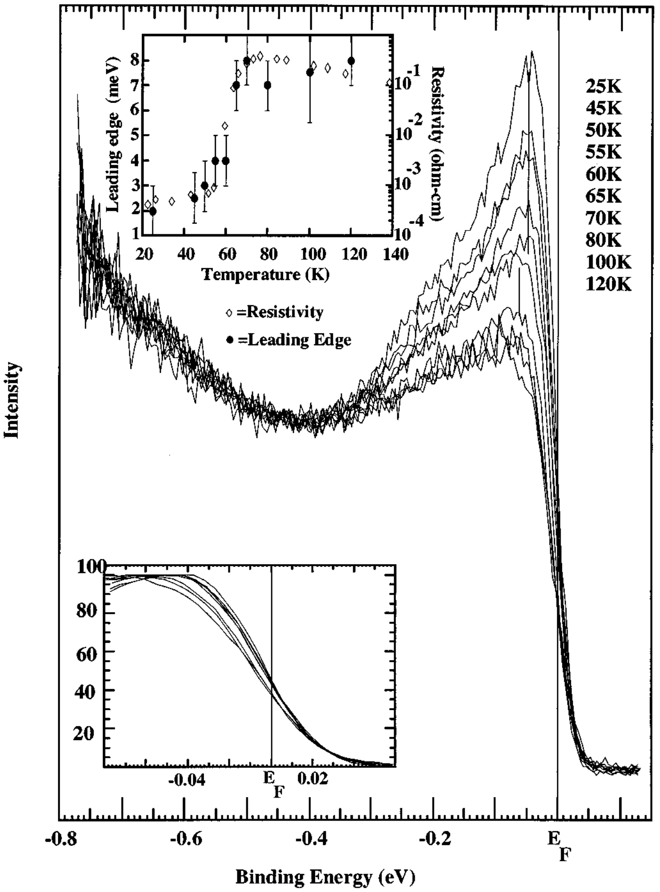

FIG. 2. Temperature dependence of the near-E_F peak at 22.4 eV incident photon energy. Upper inset: distance of the 50% point of the leading edge from E_F (filled circles) and resistivity (open diamonds, right-hand scale). Lower inset: The 22.4-eV spectra after being normalized and smoothed for analysis of the leading edge. The data fall into two clusters separated by an apparent gap, with all the metallic spectra ($T<65$ K) to the right of the apparent gap (closer to E_F), and the insulating spectra ($T>60$ K) to the left.

sudden shift of the 50% point of the near-E_F feature's leading edge at the MIT temperature, between 60 K and 65 K. In both Fig. 2 and Fig. 3, the spectra were normalized by matching spectral weight at energies above and below the near-E_F peak. This normalization procedure requires minimal ($\pm 5\%$) rescaling of the spectra. The shift was recorded at two different k-space positions, where the near-E_F feature was most intense, and the main valence band feature appeared closest to E_F.[9] This abrupt shift was not observed when the same temperature dependence experiment was performed at a k-space location where the valence-band feature appeared further from E_F, and the near-E_F feature was smaller in intensity. The shift is correlated with the MIT; we include resistivity measurements in the upper inset of Fig. 2.

Figure 3 shows 38-eV data. As in the 22.4-eV data, the near-E_F feature's intensity decreases monotonically with increasing temperature. The simple line shape allows a line-shape fitting to locate the centroid of the narrow-band peak in a consistent fashion. We fit the spectra to a Lorentzian added to a linear background and convolved with the experimental resolution function cut off by a Fermi function. Between $T=55$ K and 65 K, there is a sudden shift of the centroid (~30 meV) towards higher binding energy. In the inset of Fig. 3, we compare the centroid shift and the leading edge shift in the 38-eV data.[10] The centroid shift is an order of magnitude larger. These studies do not quantify the size of the gap but do indicate the opening of a gap.

The data in Figs. 2 and 3 constitute a direct observation of the Mott transition by photoemission. The observed shifts at the MIT temperature provide evidence that the narrow band is due to bulk rather than surface effects. The main dispersive valence-band feature at ~2.5 eV binding energy in both the $x=0$ and $x=0.5$ samples has its closest approach to E_F at an analyzer angle of 9°, where the maximum intensity of the peak near E_F occurs. This provides further evidence that the near-E_F feature is intrinsic to the material and not a consequence of surface effects.

The narrow band indicates a large effective mass and

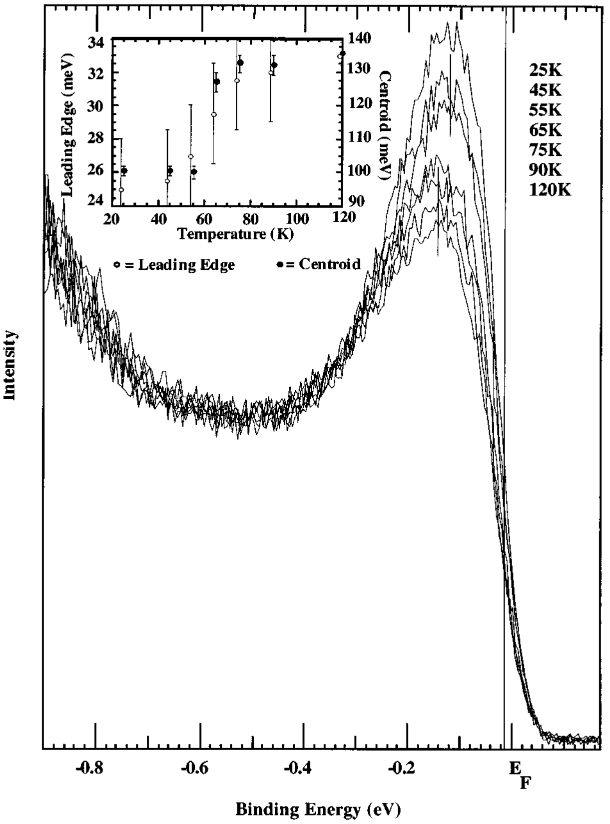

FIG. 3. Temperature dependence of the near-E_F peak at 38 eV incident photon energy. Inset: comparing the distance of the centroid from E_F (filled circles, right-hand scale) to the distance of the 50% point of the leading edge from E_F (open circles).

therefore agrees with the observed large magnetic susceptibility[11] χ and linear coefficient of the specific heat[4] γ, which are ~2.5 times and ~4 times larger for $NiS_{1.5}Se_{0.5}$ than for metallic $NiSe_2$, respectively.[12] The observed values of χ and γ are an order of magnitude larger than those of typical metals and are among the largest in non-rare-earth compounds.

The data in Figs. 2 and 3 illustrate two unusual ways in which the spectra evolve with the MIT. A narrow peak develops near E_F with Se substitution and loses spectral weight rapidly as the temperature is increased. The appearance of the narrow peak cannot be explained by one-electron band theory. This suggests that the peak is due to many-body effects. Understanding this spectral feature requires consideration of the electronic structure of the $NiS_{2-x}Se_x$ system. As often found in Mott insulators, our LDA band-structure calculation cannot reproduce the insulating ground state of NiS_2, suggesting strong correlation effects.

Figure 4(a) shows a schematic diagram of the results of LDA band calculations on NiS_2.[13] NiS_2 has a pyrite structure consisting of a fcc Ni sublattice with a S_2 dimer surrounding each Ni site.[14] According to LDA band calculations, all orbitals are completely filled except for two. The S_2 dimer forms bonding and antibonding orbitals separated by 9.5 eV. Of these, the antibonding $pp\sigma^*$ orbital is completely empty. Also, the Ni e_g bands are half filled.[15,16] However, due to strong correlation effects, the Ni $3d$ bands split into an upper ($d^8 \rightarrow d^9$) and lower Hubbard ($d^8 \rightarrow d^7$) band, separated by the large Coulomb interaction U, as illustrated in Fig. 4(b). For the Ni $3d$ bands in NiS_2, $U \approx 5$ eV.[17] According to this interpretation, NiS_2 is a charge-transfer insulator with its gap, $\Delta = 2$ eV,[17] between the filled antibonding S $pp\pi^*$ band and the empty upper $3d$ Hubbard band. The relative positions of the p and d bands are confirmed by a resonant photoemission experiment revealing that the top of the valence band has p character.[18]

Since it does not account for correlation effects, an LDA calculation does not help us to understand the MIT. However, NiS_2 is a charge-transfer insulator with a strong Coulomb U, consistent with the Zaanen-Allen-Sawatzky

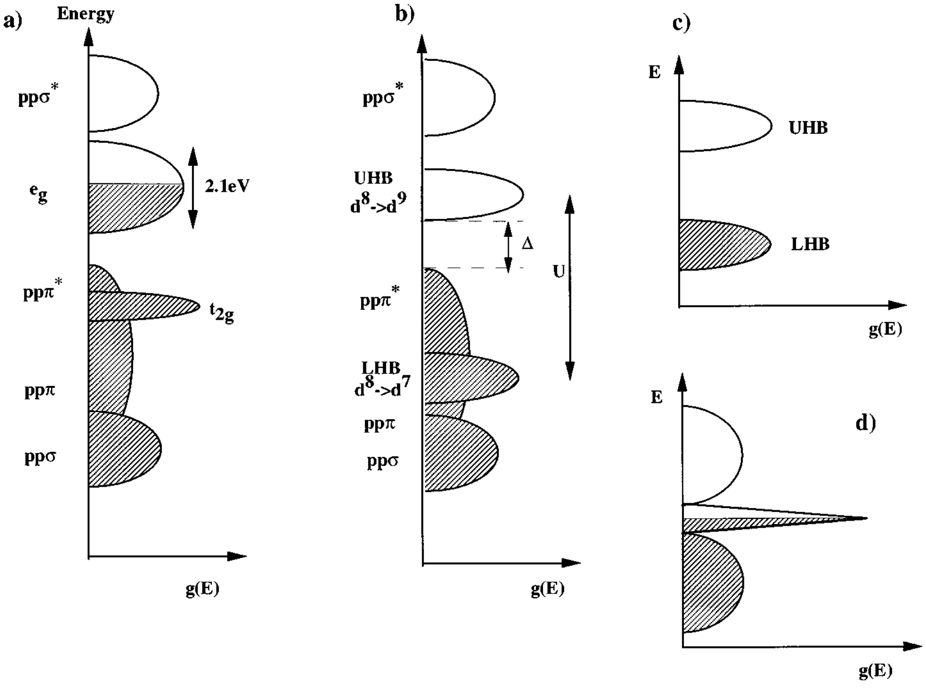

FIG. 4. (a) Band diagram of NiS_2 from LDA calculations. The energy difference between the $pp\sigma$ band and the $pp\sigma^*$ band is 9.5 eV. (b) LDA modified by Hubbard band splitting U. One-band Hubbard model in infinite dimensions: (c) insulating regime, (d) regime near MIT, i.e., where $(U/W)_{\mathrm{eff}}$ is small.

picture,[19] making it reasonable to discuss this compound using a multiband Hubbard model. By considering only the states above and below the charge-transfer gap, we may discuss the MIT qualitatively by using an effective one-band Hubbard model, with the gap (Δ) playing the role of the Coulomb U. Since the substitution of S by Se does not change the number of carriers, one can attribute the insulator-to-metal transition with increasing x to a reduction of the effective U/W ratio,[20] where W is the bandwidth.

Since the $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ MIT can be understood qualitatively by the Hubbard model, the spectral evolution in our data during the MIT provides an opportunity to test recent theoretical work on the Hubbard model. For the three-dimensional case, Hubbard provides a good solution only for the insulating regime of the MIT,[21] and the Brinkman and Rice model only considers the metallic side of the MIT.[22] Recently, several groups have worked toward a more complete picture of the MIT by solving the Hubbard model in infinite dimensions.[23–26] As U/W decreases, the Mott gap is reduced, and when U/W reaches a critical value, the system becomes metallic and can be described by three bands: the upper and lower Hubbard bands and a third narrow band in the middle of the gap at E_F.[25] Figure 4(c) illustrates the Hubbard model solution in the insulating regime, and Fig. 4(d) shows the solution for the region near the MIT. This narrow band is evident as a sharp peak in the spectral weight, which loses intensity at higher temperatures. The existence of a near-E_F peak in our data from the $x=0.5$ sample, where $(U/W)_{\mathrm{eff}}$ is small since it is metallic, agrees qualitatively with this model. In ultraviolet photoemission spectroscopy and x-ray photoemission spectroscopy experiments on V and Ti compounds, near-E_F spectral weight has been observed that appears as U/W decreases.[27] However, a sharp peak was not observed in these experiments. In our data the near-E_F peak does not disappear on the insulating side of the temperature-driven MIT, but instead we see an abrupt shift of the near-E_F peak position. A small peak has developed even before the gap closes completely to form a metal. This finding suggests that a more detailed theoretical study in the vicinity of the MIT is necessary. We note that there are differences between the $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ system and the system assumed in theoretical models. The theory assumes an $S=1/2$ system in infinite dimensions, whereas our experimental system is an $S=1$ system in three dimensions. Also, this mean-field theory does not account for the antiferromagnetic ordering, which occurs in this system at low temperature. Despite the differences between the theoretical model and the $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ system, it is interesting that our data are qualitatively consistent with predictions of the theoretical model.

The MIT with temperature is more complicated and is probably related to the volume increase and bandwidth reduction observed at the MIT temperature in the $x=0.5$ sample.[4] The abrupt increase in volume at the MIT temperature suggests a first-order MIT, which is supported by the sudden shift in the near-E_F feature in our data. A similar volume change is observed at the MIT in pure NiS_2 induced by pressure.[14]

In summary, we performed ARPES experiments on $\mathrm{NiS}_{2-x}\mathrm{Se}_x$ single crystals. We observed a sharp near-E_F peak that appears with Se substitution. This peak suddenly shifts away from E_F at the MIT temperature. A possible explanation for the appearance of this peak with Se substitution is provided by the Hubbard model in infinite dimensions.

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[1] J. A. Wilson, in *The Metallic and Nonmetallic States of Matter*, edited by P. P. Edwards and C. N. R. Rao (Taylor & Francis, London, 1985), p. 215.

[2] J. M. Honig, in *The Metallic and Nonmetallic States of Matter* (Ref. 1), p. 261.

[3] H. S. Jarrett *et al.*, Mater. Res. Bull. **8,** 877 (1973).

[4] T. Miyadai *et al.*, J. Phys. (Paris) **49**, C8-187 (1988); J. Magn. Magn. Mater. **104-7**, 1953 (1992).

[5] V. Lemos *et al.*, Phys. Status Solidi B **100**, 755 (1980).

[6] F. Gautier *et al.*, Phys. Lett. **53A**, 31 (1975).

[7] R. J. Bouchard *et al.*, Mater. Res. Bull. **8**, 489 (1973).

[8] T. Thio and J. W. Bennet, Phys. Rev. B **50**, 10 574 (1994).

[9] All the data shown in this paper were taken from the same k-space location.

[10] In the 38-eV data, the shift of the leading edge is not as abrupt as in the 22.4-eV data. This is a consequence of the relatively poor energy resolution at 38 eV. The fact that the 50% point of the leading edge in the 38-eV data is further away from E_F also can be accounted for partially by the resolution difference. The more complicated line shape of the 22.4-eV data prevents a simple line-shape fit, so it is difficult to study the centroid shift in the 22.4-eV data.

[11] S. Ogawa, J. Appl. Phys. **50**, 2308 (1979).

[12] S. Sudo, J. Magn. Magn. Mater. **114**, 57 (1992).

[13] O. Jepsen (unpublished).

[14] J. A. Wilson and G. D. Pitt, Philos. Mag. **23**, 1297 (1971).

[15] W. Folkerts *et al.*, J. Phys. C **20**, 4135 (1987).

[16] J. C. W. Folmer *et al.*, J. Solid State Chem. **72**, 137 (1988).

[17] A. E. Bocquet *et al.*, Phys. Rev. B **46**, 3771 (1992).

[18] A. Fujimori (private communication).

[19] J. Zaanen *et al.*, Phys. Rev. B **55**, 418 (1985).

[20] Here we do not consider the spin-density-wave instability at half-filling with nested Fermi surfaces.

[21] J. Hubbard, Proc. R. Soc. London Ser. A **278**, 238 (1963).

[22] W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).

[23] A. Georges and W. Krauth, Phys. Rev. B **48**, 7167 (1993).

[24] M. J. Rozenberg *et al.*, Phys. Rev. B **49**, 10 181 (1994).

[25] M. Jarrell and Th. Pruschke, Phys. Rev. B **49**, 1458 (1994).

[26] D. Vollhardt, in *Correlated Electron Systems: Proceedings of the 9th Jerusalem Winter School for Theoretical Physics*, edited by V. J. Emery (World Scientific, Singapore, 1993), p. 57.

[27] A. Fujimori *et al.* (unpublished).