ELECTRONIC STRUCTURE OF QUASICRYSTALS STUDIED BY ULTRAHIGH-ENERGY-RESOLUTION ULTRAVIOLET PHOTOEMISSION SPECTROSCOPY

Z.M. STADNIK

Department of Physics, University of Ottawa, Ottawa,
Ontario K1N 6N5, Canada

D. PURDIE, M. GARNIER, and Y. BAER

Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel,
Switzerland

A.-P. TSAI

National Research Institute for Metals, Tsukuba Laboratories,
1-2-1 Sengen, Tsukuba-Ibaraki 305, Japan

A. INOUE

Institute for Materials Research, Tohoku University,
Sendai 980, Japan

K. EDAGAWA

Institute of Industrial Science, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106, Japan

S. TAKEUCHI

Department of Materials Science and Technology, Science University of Tokyo,
Noda, Chiba 278, Japan

The results of low-temperature, ultrahigh-energy-resolution ultraviolet photoemission spectroscopy studies of the electronic structure of most known stable icosahedral and decagonal alloys are presented. It is shown that these alloys have a clearly developed Fermi edge, and are thus metallic down to the temperature of measurement ($\sim$10 K). The existence of the theoretically predicted pseudogap at the Fermi level is confirmed. With an experimental resolution of 5 meV, no evidence of the theoretically predicted spikiness of the density of states could be observed. The experimental results are discussed in relation to various theoretical models which attempt to explain some of the unusual physical properties of quasicrystals

1   Introduction

The physical properties of icosahedral (i) alloys are very unusual.[1] Their most salient feature, which is completely unexpected for alloys consisting of normal metallic elements, is the very low value of the electrical conductivity σ.

While the low-temperature σ values of the Al-Cu-TM (TM=Fe,Ru,Os) i alloys [2-5] are in the range 20–100 $\Omega^{-1}cm^{-1}$, those of the Al-Pd-Re i alloys are very close to zero. [6-8] These low-temperature σ values are significantly smaller than the Mott's "minimum metallic conductivity" of 200 $\Omega^{-1}cm^{-1}$ for the metal-insulator transition. The Al-Cu-TM were labelled "marginally metallic" or "semiconducting" (Refs. 9-10), whereas the Al-Pd-Re alloys were called insulators. [6,9] Some other unexpected physical properties of i alloys involve [1] the positive temperature coefficient of σ, extreme sensitivity of σ to the sample composition, decrease of σ as the structural quality of i alloys improves, a very low electronic contribution to the specific heat, and large and strong temperature-dependent Hall coefficient and thermoelectric power. From a magnetic point of view, i alloys of high structural quality are unusual in that they are diamagnetic in spite of containing significant concentration of TM atoms.

The alloys of decagonal (d) symmetry exhibit anisotropic physical properties of various physical parameters. [1] Their electrical resistivity has metallic characteristics along the periodic direction, and shows a nonmetallic behavior in the quasiperiodic plane. The d alloys alloys Al-Co-Cu and Al-Co-Ni are diamagnetic over a wide temperature range.

At present there is no well-established theory which would account for the observed unusual physical properties of quasicrystals (QC's). [1] Conventional approaches are based on band-structure effects and the Hume-Rothery rule, and imply the existence of a pseudogap in the density of states (DOS) at the Fermi level E_F and a very spiky structure of the DOS. [11,12] While the pseudogap can be related to the stability and low value of σ, the spiked structure of the DOS is believed to be a signature of quasiperiodicity and to be responsible for several unusual temperature-dependent transport properties. More exotic mechanisms, which invoke the concepts of tunneling, localization, critical states, and fractons, [1,13] have been recently proposed to explain the unusual transport properties of QC's.

In order to directly and unambiguously determine the metallic or nonmetallic character of the i alloys and to verify the hypothesis of the pseudogap and the DOS spikiness, photoemission spectroscopy (PES) measurements with ultrahigh energy resolution are essential. [14] Furthermore, they have to be performed at low temperatures where thermal broadening of the Fermi-Dirac function is small so that an instrumental contribution to broadening is of the same order of magnitude as $k_B T$. [15] In this paper we report the main results of an extensive study of the electronic structure of most known stable QC's, where it is demonstrated that only through use of these stringent experimental conditions can firm conclusions regarding the detailed form of the near-E_F

DOS be drawn.

2 Experimental

Thermodynamically stable i and d alloys of nominal compositions $Al_{65}Cu_{20}Fe_{15}$, $Al_{64}Cu_{24}Fe_{12}$, $Al_{65}Cu_{20}Ru_{15}$, $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$, $Al_{65}Cu_{20}Os_{15}$, $Al_{70}Pd_{20}Mn_{10}$, $Al_{70}Pd_{20}Cr_5Fe_5$, $Al_{70.5}Pd_{21}Re_{8.5}$, $Zn_{60}Mg_{32}Y_8$, $Al_{65}Co_{15}Cu_{20}$, and $Al_{70}Co_{15}Ni_{15}$ were prepared as described elsewhere.[1,5] All samples were characterized by X-ray diffraction and electron microscopy, both techniques showing the samples to be single phase. Bragg-peak widths were resolution-limited.

The samples were mounted on the cold finger of a liquid He cryostat and, while held at the lowest measurement temperature, were cleaned *in situ* ($\sim$ 10^{-10} Torr) by repeated scraping with a diamond file until no surface contamination could be detected. Valence band spectra obtained from different regions of a given sample, as well as from several samples corresponding to a given composition, were reproducible. We therefore believe that the spectra are representative of the intrinsic features of the QC's studied. The ultraviolet photoelectron spectroscopy (UPS) spectrometer was equipped with a high-intensity He discharge lamp (Gammadata) producing a He I line at 21.2 eV and a He II line at 40.8 eV, and a high-resolution Scienta SES200 hemispherical analyzer. The instrumental resolution was determined by fitting the Fermi edge of Ag, evaporated *in situ* onto the previously measured samples, with the convolution of a Gaussian and the product of a linear DOS and the Fermi-Dirac function at the appropriate temperature.[15] The FWHM of the Gaussian is the only adjustable parameter in this procedure and gives directly the instrumental resolution. For ultrahigh resolution spectra this was determined to be ≤ 10 meV. The uncertainty in the determination of E_F is less than 0.5 meV. The UPS valence bands presented here are corrected for the secondary-electron background.[14]

3 Results and Discussion

3.1 Structure of Valence Bands

The low-temperature He II valence bands of some representative i and d alloys (Fig. 1) have a two-peak structure. The feature at the binding energy of about -4.1 eV is mainly due to the Pd 4d- or Cu 3d-derived states, whereas the feature close to E_F is predominantly due to states of Mn, Fe, Co, Ni 3d, Ru 4d, or Re 5d character. This assignment is based upon previous resonance PES studies of QC's.[14,16]

There are two salient features of the valence bands of stable QC's (Fig. 1 and Ref. 1). First, the presence of the Fermi edge is indicated in all studied QC's. Second, as compared to that of other QC's, a significantly lower spectral intensity at E_F is observed in the Al-Pd-Re i alloy.
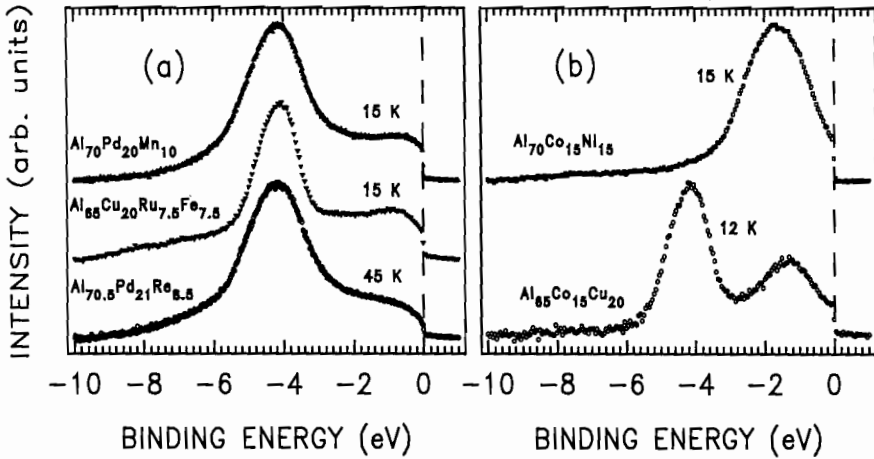

Figure 1: Low-temperature He II valence bands of (a) i alloys and (b) d alloys. The energy resolution is ~30 meV. The spectra have been normalized to give a constant height between the maximum and minimum count.

3.2   Valence Bands in the Vicinity of E_F

The valence band region of QC's close to E_F was examined with the highest energy resolution available to us. [1,17] As an example, a high-energy-resolution spectrum for the i alloy $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$ is shown in Fig. 2(a). A clearly developed Fermi edge, which can be perfectly fitted using a Fermi-Dirac function convoluted with a Gaussian function representing the instrumental broadening [Fig. 2(a)], is observed. Its temperature evolution follows exactly that of a Fermi-Dirac function [Fig. 2(b)].

The near-E_F spectra of i $Al_{70.5}Pd_{21}Re_{8.5}$ also exhibit the presence of a Fermi edge. This can be seen by comparing a near-E_F spectrum at 45 K of $Al_{70.5}Pd_{21}Re_{8.5}$ with that of Ag evaporated onto the alloy [Fig. 2(c)]. This is also evidenced by the fits of the spectra of this alloy measured at 45 and 9 K [Fig. 2(c)].

Spectra like those in Fig. 2 were also observed for other studied i and d

alloys. [1,17] This constitutes a direct and convincing proof that these QC's, in spite of their unusually low values of σ, are metallic down to the temperature of measurement (9 K). Labeling such QC's "marginally metallic", "semiconducting", or "insulating" is not, therefore, justified.
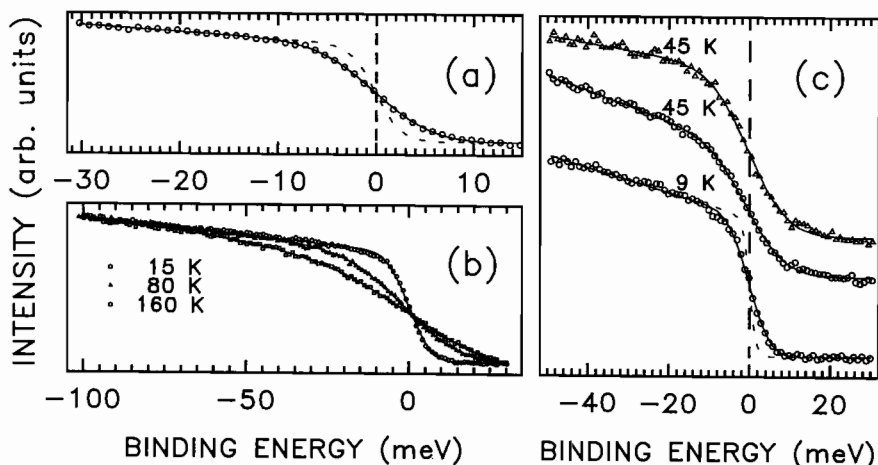

Figure 2: (a) Near-E_F He I valence band of $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$ at 15 K. The solid line is a fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 15 K (broken curve) and convoluted with a Gaussian whose FWHM is equal to 9.8(2) meV. Note that the step between the data points is 1 meV. (b) Near-E_F He I valence bands of $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$ measured at various temperatures. The solid lines are the fits as described in (a). Note the different binding energy scales in (a) and (b). (c) Near-E_F He I valence bands of $Al_{70.5}Pd_{21}Re_{8.5}$ (circles) and Ag (triangles) evaporated onto it at 45 and 9 K. The solid and broken curves are respectively the fits and the Fermi-Dirac function at 9 K, as described in (a). The Gaussian FWHM is respectively 6.0(5) and 9.2(3) meV for the spectra measured at 45 and 9 K.

3.3 Pseudogap in DOS around E_F

In order to verify convincingly the hypothesis of a pseudogap around E_F with an experimental technique which probes the occupied electronic states directly, it is essential to distinguish between the decrease of the spectral intensity toward E_F, which results from the presence of a pseudogap, and the Fermi-edge cutoff. Such a distinction could not be achieved with previous low-energy resolution, room-temperature PES studies. [1] The spectral intensity decrease

toward E_F is clearly separated from the Fermi-edge cutoff in the present high-energy-resolution, low-temperature UPS spectra (Figs. 1–3).
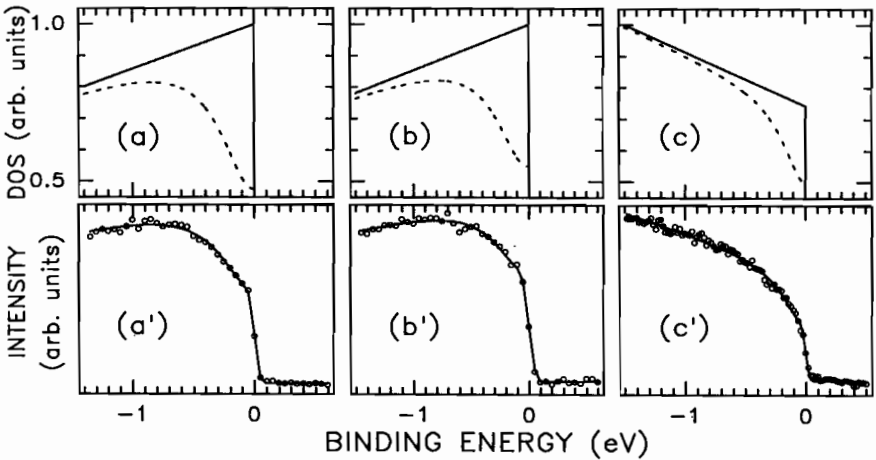

Figure 3: The model of the DOS at 0 K which is used to fit the region of the valence band close to E_F for (a) $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$, (b) $Al_{70}Pd_{20}Cr_5Fe_5$, and (c) $Al_{70.5}Pd_{21}Re_{8.5}$. The solid lines represent the normal DOS at 0 K, whereas the broken lines represent the Lorentzian dip which must be subtracted from the normal DOS in order to fit [solid lines in (a'), (b'), and (c')] the corresponding regions of the valence bands close to E_F [circles in (a'), (c'), and (b') are the experimental points from Fig. 1(a) ($Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$ and $Al_{70.5}Pd_{21}Re_{8.5}$) and from Ref. 1 ($Al_{70}Pd_{20}Cr_5Fe_5$), respectively].

With the aim of obtaining simple parameters to characterize the pseudo-gap, one can simulate the observed structure close to E_F in the valence bands of the studied QC's using the model proposed by Mori *et al.* (Ref. 18). As conventional alloys of the quasicrystal-forming elements do not display a DOS minimum close to E_F, it is assumed that a simple linear extrapolation of the spectra for the binding energy range directly before the peak of the valence band feature close to E_F accounts for the DOS without the pseudogap (the normal DOS).[18] The presence of the pseudogap would result in an intensity dip which is assumed to be of Lorentzian shape centered at E_F, character-ized by the half-width, Γ_L, and the dip depth relative to the normal DOS, C. Thus, the observed intensity is the convolution of the normal DOS multiplied by the pseudogap Lorentzian function and by the Fermi-Dirac function, and the experimental resolution Gaussian function. The C values of 0 and 100 % correspond respectively to the normal DOS (no pseudogap) and no DOS(E_F).

The application of the dip model to account for the shape of the valence band regions close to E_F for i alloys $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$, $Al_{70}Pd_{20}Cr_5Fe_5$, and $Al_{70.5}Pd_{21}Re_{8.5}$ is presented in Fig. 3. The model is in good agreement with the experimental data close to E_F both of i alloys (Fig. 3 and Ref. 1) and of d alloys (Ref. 1).

The analysis of UPS spectra close to E_F leads to three observations.[1] First, the available electronic structure calculations for the approximants of the i alloys Al-Cu-Fe (Ref. 11) and Al-Pd-Mn (Ref. 12) relevant to the present study predict values of Γ_L of a few tenths of eV. This agrees with the values determined for i alloys $Al_{65}Cu_{20}Fe_{15}$, $Al_{64}Cu_{24}Fe_{12}$, and $Al_{70}Pd_{20}Mn_{10}$ alloys.[1] Second, the electronic structure calculations for the approximant of the d alloy Al-Co-Cu (Ref. 19) predict a much wider pseudogap ($\sim$1 eV). The Γ_L values of about 1 eV are observed[1] for the d alloys $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$. Third, one would expect to observe a correlation between C, which is a measure of $1/DOS(E_F)$, and σ assuming that the Hume-Rothery type mechanism is the main reason for the observed low values of σ in i alloys. Such a correlation is not observed. Similar values of C are found for i alloys whose values of σ differ by several orders of magnitude.[1] This supports the idea that the Hume-Rothery mechanism cannot be the major cause of the low values of σ.

3.4 Fine Structure of DOS

The predicted DOS spikiness should be detectable in high- and ultrahigh-energy-resolution PES experiments for binding energies up to about 3 eV below E_F (Ref. 1). An inspection of the valence bands measured with high- (Figs. 1 and 3) and ultrahigh- (Fig. 2) energy resolution shows the lack of any fine structure.

The failure to detect the predicted DOS spikiness suggests the presence of some disorder even in the structurally "perfect" (phason free) QC's. Such disorder is expected to smear out the fine structure of the DOS. There are some experimental facts which support this suggestion. First, local probes, such as Mössbauer spectroscopy, NMR, and nuclear quadrupole resonance,[20] clearly show the presence of distributions of the hyperfine parameters in the structurally perfect QC's. Such distributions can only occur if there is chemical/topological disorder in the samples. Second, diffuse scattering is often observed in X-ray, electron, and neutron diffraction patterns of high-quality poly-quasicrystalline and single-grain QC's. Its presence indicates that some disorder must be present in the diffracting structure. Third, the success of quantum interference theories, which were originally developed for disordered conductors, in accounting for the temperature and field dependencies of σ and

magnetoresistance of several stable i alloys indicates that these alloys are electronically disordered.

Acknowledgments

References

1. Z.M. Stadnik *et al.*, *Phys. Rev.* B **55**, 10938 (1997).
2. T. Klein *et al.*, *Phys. Rev. Lett.* **22**, 2907 (1991).
3. P. Lanco *et al.*, *Europhys. Lett.* **18**, 227 (1992).
4. B.D. Biggs *et al.*, *Phys. Rev. Lett.* **21**, 2700 (1990).
5. Y. Honda *et al.*, *Jpn. J. Appl. Phys.* A **34**, 2415 (1995).
6. F.S. Pierce *et al.*, *Phys. Rev. Lett.* **73**, 2220 (1994).
7. Y. Honda *et al.*, *Jpn. J. Appl. Phys.* A **33**, 4929 (1994).
8. C Gignoux *et al.* in *Proceedings of the 5th International Conference on Quasicrystals*, ed. C Janot and R Mosseri (World Scientific, Singapore, 1995), p. 452.
9. D.N. Basov *et al.* in *Proceedings of the 5th International Conference on Quasicrystals*, ed. C Janot and R Mosseri (World Scientific, Singapore, 1995), p. 564.
10. R. Tamura *et al.*, *Phys. Rev.* B **50**, 9640 (1994).
11. G. Trambly de Laissardière and T. Fujiwara, *Phys. Rev.* B **50**, 5999 (1994).
12. M. Krajčí *et al.*, *Phys. Rev.* B **51**, 17355 (1995).
13. G. Trambly de Laissardière and D. Mayou, *Phys. Rev.* B **55**, 2890 (1997).
14. Z.M. Stadnik *et al.*, *Phys. Rev.* B **51**, 4023 (1995).
15. M. Grioni *et al.*, *J. Low Temp. Phys.* **99**, 195 (1995).
16. Z.M. Stadnik *et al.*, *Phys. Rev.* B **51**, 11358 (1995).
17. Z.M. Stadnik *et al.*, *Phys. Rev. Lett.* **77**, 1777 (1996).
18. S. Mori *et al.*, *J. Phys. Condens. Matter* **3**, 767 (1991).
19. G. Trambly de Laissardière and T. Fujiwara, *Phys. Rev.* B **50**, 9843 (1994).
20. Z M Stadnik in *Mössbauer Spectroscopy Applied to Magnetism and Materials Science*, ed. G J Long and F Grandjean (Plenum, New York, 1996), p. 125.