

Pseudogap in Quasicrystals Studied with Photoemission Spectroscopy

Zbigniew Marian Stadnik

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

The results of the low-temperature, high energy resolution photoemission studies of a single-grain icosahedral alloy $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ have been presented. The existence of the theoretically predicted pseudogap has been confirmed. No evidence of the theoretically predicted spikiness of the density of states could be observed. A review of published experimental data on the electronic structure of quasicrystals has also been presented. The photoemission experimental results confirm the existence of a pseudogap in the density of states in icosahedral quasicrystals, but its existence in the decagonal quasicrystals remains still an open question. The predicted DOS spikiness could not be observed in any of the studied quasicrystals.

(Received January 18, 2001; Accepted March 19, 2001)

Keywords: quasicrystals, icosahedral alloys, decagonal alloys, electronic structure, pseudogap

1. Introduction

Quasicrystals (QCs) are a new form of the solid state which differs from the other two known forms, crystalline and amorphous, by possessing a new type of long-range translational order, *quasiperiodicity*, and a noncrystallographic orientational order associated with the classically forbidden fivefold (icosahedral), eightfold (octagonal), tenfold (decagonal) and twelvefold (dodecagonal) symmetry axes.¹⁾ One of the central problems in condensed-matter physics is to determine whether quasiperiodicity leads to physical properties which are significantly different from those of crystalline and amorphous materials of the same/similar compositions.

The physical properties of QCs, and especially their electronic transport properties, are very unusual.¹⁾ They are ultimately determined by the electronic structure of these alloys. Knowledge and understanding of the electronic structure are thus essential if we are to understand the unexpected physical properties of QCs.

There are three major theoretical predictions of the electronic structure of icosahedral (I) and decagonal (D) alloys. The first one is the prediction of the existence of the pseudogap in the density of states (DOS) at the Fermi level E_F . The early calculations based on the nearly-free-electron approximation concluded²⁻⁸⁾ that such a pseudogap should exist in the I alloys. Modern electronic structure calculations performed for the approximants to various I alloys unanimously predict the presence of the pseudogap in the DOS(E_F).⁹⁻²³⁾ This is illustrated in Fig. 1 which shows the predicted DOS for the 1/1 approximant to the I Al-Pd-Mn alloy.¹⁷⁾ For D alloys, the theoretical predictions concerning the existence of a pseudogap at the DOS(E_F) are controversial. Some calculations postulate the existence of such a pseudogap^{24,25)} in the D Al-Cu-Co alloys. This has been disputed in other theoretical studies.²⁶⁻²⁸⁾ The electronic-structure calculations for approximants to the D Al-Pd-Mn system predict that a pseudogap exists only in the Al-*sp* band.^{29,30)} For the D Al-Ni-Co alloys it is predicted that no pseudogap exists in the DOS(E_F).³¹⁾

The second theoretical prediction of the electronic structure calculations carried out for various approximants to QCs is the fine structure (spikiness) of the DOS (Fig. 1).^{9-24,26-31)}

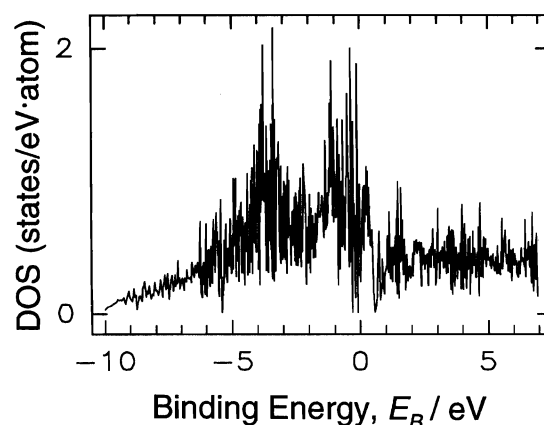


Fig. 1 Theoretical DOS for the 1/1 approximant to the I Al-Pd-Mn alloy.¹⁷⁾

The DOS of QCs is believed to consist of many very fine spiked peaks with a width of about 10 meV. This spikiness is invoked¹⁾ to explain the experimental observation that the electrical resistivity ρ of QCs is unusually sensitive to slight changes in their composition: such changes shift the position of E_F , resulting in a strong change of the DOS(E_F), and consequently of ρ .

The predicted minimum of DOS(E_F) (a pseudogap) is not a unique characteristic which distinguishes the electronic structure of QCs from that of crystalline and amorphous alloys since the pseudogap does occur in both crystalline and amorphous systems.¹⁾ However, the predicted DOS spikiness seems to be such a unique property which distinguishes QCs from crystalline and amorphous alloys.

The third important result of the band-structure calculations is the prediction²²⁾ of the possible existence of a real gap in the DOS around E_F in the I Al-Pd-Re system.

The anomalously large ρ and a low electronic specific heat coefficient γ were taken as an experimental evidence for the existence of a pseudogap in the DOS at E_F .³²⁻³⁵⁾ A universal experimental relation $\rho \sim \gamma^{-1/2}$, discovered independently by Mizutani³⁴⁾ and Rapp³⁵⁾ for many I alloys, is indicative of the minimum of the DOS(E_F) in these alloys. The results of the NMR,³⁶⁻³⁹⁾ optical conductivity⁴⁰⁻⁴⁵⁾ and photoconductiv-

ity⁴⁶⁾ experiments were interpreted in terms of the pseudogap in the DOS(E_F) in the I alloys.

For D alloys, contradictory conclusions had been drawn from the results of various experiments regarding the possible existence of the pseudogap. The Hall-effect⁴⁷⁾ and magnetic susceptibility⁴⁸⁾ measurements of D Al–Ni–Co and Al–Cu–Co alloys were interpreted in terms of a pseudogap in the DOS(E_F). The low values of γ measured for the D Al–Cu–Co⁴⁹⁾ and Al–Ni–Co⁵⁰⁾ alloys were interpreted as indicative of a pseudogap in the DOS(E_F). The presence of a pseudogap at E_F in the DOS in the D Al–Ni–Co⁵⁰⁾ alloy and its absence in the D Al–Cu–Co alloys⁵¹⁾ were inferred from the analysis of the optical conductivity results.

A common characteristic of the measurements briefly reviewed above is the fact that they probe the DOS *indirectly* via, sometimes complex, dependence of the measured parameters upon DOS. Studies using spectroscopic techniques which probe DOS *directly* in the vicinity of E_F are therefore desirable to determine whether the pseudogap in the DOS occurs in QCs. I shall present in this paper the results of the high-resolution photoemission spectroscopy (PES) measurements on a single-grain Al–Pd–Mn alloy and review the results obtained for other QCs.

2. Experimental Procedure

Thermodynamically stable polyquasicrystalline I and D alloys were prepared as described elsewhere.⁵²⁾ All polyquasicrystalline 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 preparation of the single-grain I Al₇₀Pd_{21.5}Mn_{8.5} used in the ultraviolet photoelectron spectroscopy (UPS) study⁵³⁾ has been described elsewhere.⁵⁴⁾ Its surface was oriented within 0.25° perpendicular to the fivefold axis. An inspection of the sample for the presence of second phases using scanning electron and scanning Auger microscopy indicated that, within a detection limit of 1%, the sample is single phase. The surface of the fivefold single-grain I Al₇₀Pd_{21.5}Mn_{8.5} was prepared for the UPS experiments by sputtering-annealing cycles. Annealing periods were typically 30 min during cleaning and several hours before the UPS experiments. Annealing was done at 773 K⁵⁵⁾ which yielded a clear fivefold low-energy electron diffraction pattern.⁵³⁾

High-resolution PES experiments at various temperatures were carried out in an angle-integrated mode using an UPS spectrometer equipped with a high-intensity He discharge lamp (Gammadata) producing a He I line at 21.2 eV and He II line at 40.8 eV, and a high-resolution Scienta SES200 hemispherical analyzer.⁵²⁾ The instrumental resolution was determined by fitting the Fermi edge of Ag, evaporated *in situ* onto the previously measured sample, with the convolution of a Gaussian and the product of a linear DOS and the Fermi-Dirac function at the appropriate temperature.⁵⁶⁾ The full width at half-maximum (FWHM) of the Gaussian is the only adjustable parameter in this procedure and gives directly the instrumental resolution. Room-temperature PES measurements with medium energy resolution were carried out with different photon energies $h\nu$ using the synchrotron radiation.⁵⁷⁾ The PES valence bands presented here are cor-

rected for the secondary-electron background.⁵⁷⁾

3. Results and Discussion

3.1 Pseudogap in icosahedral quasicrystals

The low-temperature He II valence band the single-grain sample I Al₇₀Pd_{21.5}Mn_{8.5} [Fig. 2(a)] differs from the corresponding valence band of a polyquasicrystalline I Al₇₀Pd₂₀Mn₁₀ sample⁵⁸⁾ in that the main feature at the binding energy E_B of -4.1 eV of the former has a clear shoulder at $E_B \approx -5$ eV. The main feature of the valence band is mainly due to the Pd 4*d*-derived states, whereas the feature close to E_F is predominantly due to states of Mn 3*d* character. This assignment is based on previous room-temperature synchrotron-radiation PES studies^{59,60)} carried out on the polyquasicrystalline I Al₇₀Pd₂₀Mn₁₀ sample with an energy resolution of 400 meV. They established a good agreement between the theoretical and experimental partial DOS of the Mn 3*d* and Pd 4*d* character (Fig. 3) and the total experimental and theoretical DOS (Fig. 4).

As in the case of polyquasicrystalline I Al₇₀Pd₂₀Mn₁₀,⁵⁸⁾ a clearly developed Fermi edge is observed for the single-grain I Al₇₀Pd_{21.5}Mn_{8.5} alloy [Fig. 2(b)]. This constitutes a direct proof that this alloy, in spite of its high ρ ,³⁵⁾ is metallic.

The decrease of the spectral intensity towards E_F [Fig. 2(a)], which is clearly distinguished from the decrease due to the Fermi cut-off, results from the presence of a pseudogap in the DOS(E_F). With the aim of obtaining simple parameters to characterize the pseudogap, one can simulate the observed structure close to E_F in the valence band using the model proposed by Mori *et al.*⁶¹⁾ 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 spectrum for E_B energy range directly before the

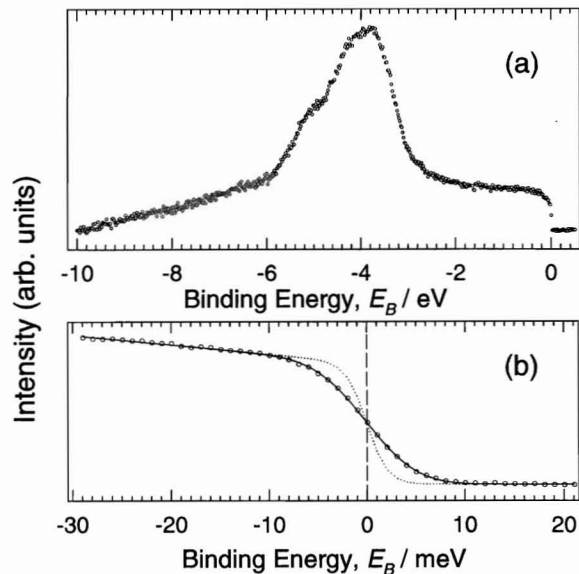


Fig. 2 (a) He II angle-integrated valence band of the single-grain I Al₇₀Pd_{21.5}Mn_{8.5} at 12 K measured with an energy resolution of 8.6(1) meV. (b) Near- E_F He I angle-integrated valence band of the single-grain I Al₇₀Pd_{21.5}Mn_{8.5} at 12 K. The solid line is the fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 12 K (broken curve) and convoluted with a Gaussian whose FWHM = 8.6(1) meV. Note the different binding energy scales in (a) and (b).

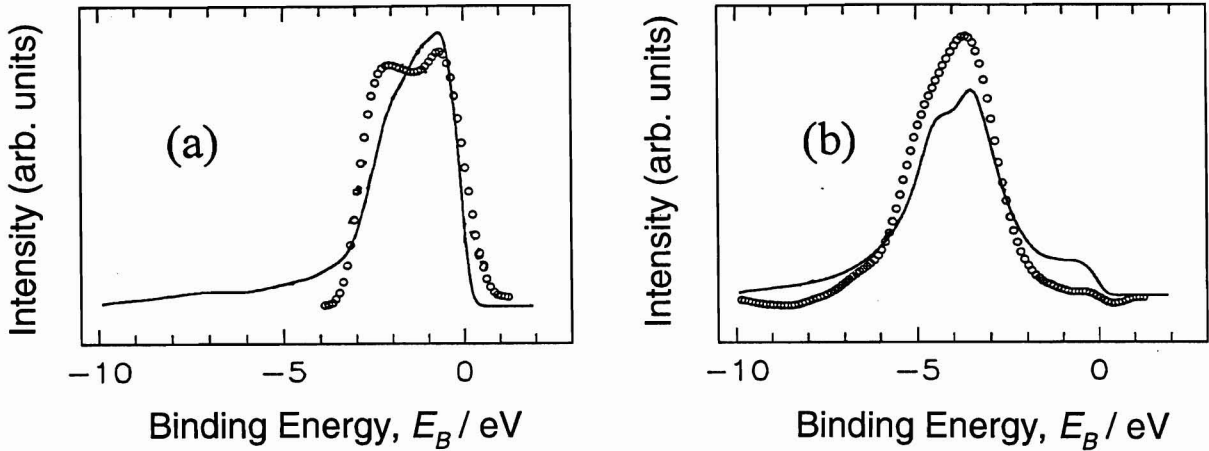


Fig. 3 Comparison of the partial DOS in the I Al₇₀Pd_{21.5}Mn_{8.5} alloy of the (a) Mn 3d and (b) Pd 4d character obtained from the PES spectra measured with an energy resolution of 400 meV (open circles⁶⁰) with the corresponding broadened theoretical partial DOS (solid line¹⁷).

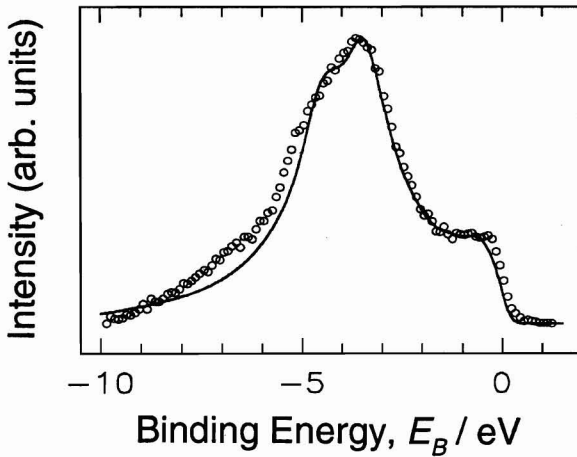


Fig. 4 Comparison of the room-temperature valence band of the I Al₇₀Pd_{21.5}Mn_{8.5} alloy measured at $h\nu = 100$ eV with an energy resolution of 400 meV (open circles⁵⁹) with the broadened theoretical DOS for the 8/5 approximant to the I Al–Pd–Mn alloy (solid line¹⁷).

peak in the valence band feature close to E_F accounts for the DOS without the gap (the normal DOS). The presence of a pseudogap would result in an intensity dip which is assumed to be of Lorentzian shape centered at E_F , characterized by the half-width Γ_L , and the dip depth relative to the normal DOS, C . The observed intensity $I(E_B)$ is the convolution of the normal DOS multiplied by the pseudogap Lorentzian function and by the Fermi-Dirac function $f(E_B, T)$, and the experimental resolution Gaussian function

$$I(E_B) = \int N(ax + b) \left(1 - \frac{C\Gamma_L^2}{x^2 + \Gamma_L^2} \right) f(x, T) \times \exp \left[-\frac{(x - E_B)^2}{2s^2} \right] dx, \quad (1)$$

where N is a normalization factor, the experimental Gaussian FWHM is related to s through $\text{FWHM} = 2\sqrt{2 \ln 2} s$, and the constants a and b are determined from a linear fit of the spectrum for E_B energy range between -1.2 to -0.7 eV. The C values of 0 and 100% correspond, respectively, to the normal DOS (no pseudogap) and no DOS(E_F). There is some

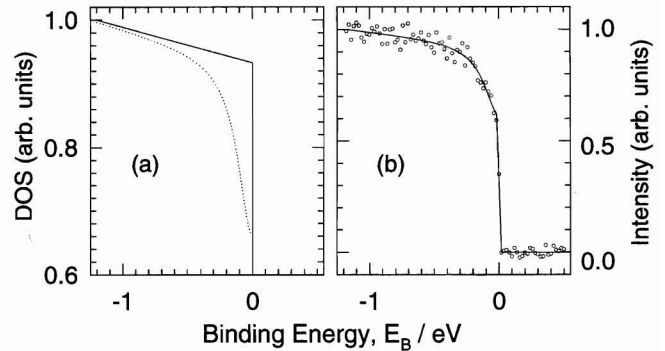


Fig. 5 (a) The model of the DOS at 0K which is used to fit the near- E_F region of the angle-integrated valence band of single-grain I Al₇₀Pd_{21.5}Mn_{8.5} at 12 K from Fig. 2(a). The solid line represents the normal DOS at 0K, whereas the broken line represents the dip which must be subtracted from the normal DOS in order to fit the near- E_F region of the valence band. (b) The near- E_F region of the angle-integrated valence band of single-grain I Al₇₀Pd_{21.5}Mn_{8.5} at 12 K from Fig. 2(a) (open circles) fitted (solid line) to the model DOS shown in (a) which is multiplied by the Fermi-Dirac function at 12 K and convoluted with the experimental Gaussian function of FWHM = 8.6 meV.

arbitrariness in the model expressed by eq. (1) regarding the choice of the E_B range for which the data are fitted to a line $aE_B + b$ representing a normal DOS, which results in not unique values C and Γ_L characterizing the pseudogap. Nevertheless, one obtains a reasonable estimate of the width and depth of the pseudogap with this procedure. A good fit of the near- E_F region of the valence band of the single-grain I Al₇₀Pd_{21.5}Mn_{8.5} alloy [Fig. 5(b)] with this model [Fig. 5(a)] is achieved for parameter values $C = 33.9(1.9)\%$ and $\Gamma_L = 0.13(1)$ eV. The values of these parameters obtained from the similar fit of the near- E_F region of the valence band of the polyquasicrystalline I Al₇₀Pd₂₀Mn₁₀ alloy⁵⁸) are respectively 28.1(1.0)% and 0.22(2) eV. It can thus be concluded that the high-resolution UPS data obtained from both polyquasicrystalline and single-grain samples are in support of the theoretically predicted¹⁷) presence of the pseudogap in the I Al–Pd–Mn system.

The near- E_F region of the valence bands of other polyquasicrystalline I alloys measured at low temperatures with high-resolution UPS technique⁵²) could be successfully an-

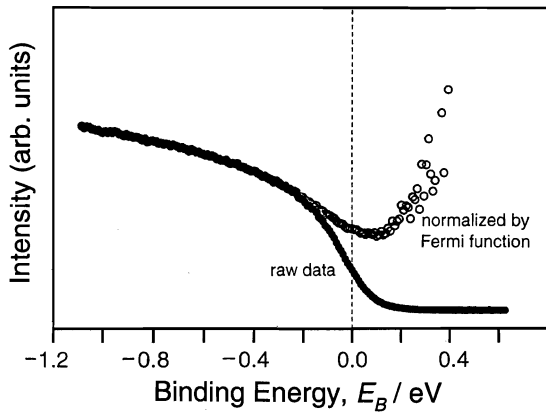


Fig. 6 Angle-integrated valence band of single-grain I Al_{70.5}Pd₂₁Mn_{8.5} at 570 K measured at $h\nu = 32.3$ eV with an energy resolution of 70 meV (full circles) and the reconstructed spectral function (open circles) near E_F .⁶³⁾

alyzed with eq. (1). This was taken as evidence for support of the existence of the pseudogap in these I alloys.⁵²⁾

PES valence bands probe directly the DOS below E_F .⁶²⁾ To unambiguously reveal the presence of a pseudogap around E_F , the states above E_F must also be investigated. This is normally achieved by using the inverse photoemission spectroscopy (IPES) technique.⁶²⁾ However, the PES technique can also probe the states above E_F if they are populated. According to Fermi-Dirac statistics, in metallic systems these states become populated at non-zero temperatures. At high temperatures (~ 600 K), a region of several hundred meV above E_F becomes accessible. Such a PES study, with an energy resolution of 70 meV, was carried out on the single-grain I Al_{70.5}Pd₂₁Mn_{8.5}, whose surface was perpendicular to the fivefold axis, at 570 K.⁶³⁾ A spectral function, which is proportional to the DOS, can be reconstructed from such a valence band. It clearly shows (Fig. 6) a minimum of DOS located at 90 meV above E_F .⁶³⁾ For E_B values higher than ~ 300 meV ($6.1 k_B T$), a considerable scatter of the reconstructed spectral function, which is due to the small probability that the states are populated, prevents a meaningful evaluation of the DOS. Accessing states slightly above E_F through the method described above is superior to IPES because of the much higher energy resolution of the PES experiment.⁶³⁾

PES and IPES measurements were combined in the study of the I Al₅₅Li_{35.8}Cu_{9.2} alloy and the 1/1 approximant Al₅₄Li_{36.8}Cu_{9.2} to the I Al-Li-Cu I phase (R phase).⁶⁴⁾ A decrease of the spectral intensity close to E_F [(Fig. 7(a))] could not be interpreted as resulting from the presence of a pseudogap since it could not be distinguished from the decrease due to the Fermi energy cut off caused by the limited energy resolution (700 and 400 meV respectively for the $h\nu = 100$ and 40 eV valence bands) of the PES experiment.⁶⁴⁾ However, a reasonable agreement between the calculated PES spectra¹⁵⁾ and the measured valence bands, in particular concerning the existence of the reduced DOS at E_F [Fig. 7(b)], is indicative that the observed decrease of the spectral intensity close to E_F [(Fig. 7(a))] is also caused by the presence of the pseudogap in these alloys. A comparison between the IPES spectra of the I Al₅₅Li_{35.8}Cu_{9.2} alloy and the R phase Al₅₄Li_{36.8}Cu_{9.2} measured with an energy resolution of 700 meV (Fig. 8) shows that the pseudogap is opening slightly above E_F and that it is

shallower in the latter than in the former. A combination of PES and IPES spectra thus establishes that, as predicted by theory,¹⁵⁾ there is a pseudogap in the DOS in the I Al-Li-Cu system and the R phase.

The PES and IPES data on the occupied and unoccupied DOS provides conclusive evidence for the presence of the theoretically predicted pseudogap in the Al-Li-Cu and Al-Pd-Mn I alloys. For other investigated I alloys, the data are compatible with the presence of the pseudogap. A generally good agreement between the calculated and measured DOS indicates that the essential ingredients of the electronic structure of I alloys can be obtained from the calculations carried out for their approximants.

The I Al-Pd-Re alloys exhibit the highest ρ of all known QCs³⁵⁾ and it was suggested that they are insulators at low temperatures. Contradictory claims were made concerning the possibility of the I Al-Pd-Re alloy being an insulator based on the interpretation of the electronic transport data.⁶⁵⁻⁶⁹⁾ The low-temperature near- E_F He I valence bands of I Al_{70.5}Pd₂₁Re_{8.5} measured with the highest energy resolution presently available (Fig. 9) clearly show the presence of a Fermi edge.⁷⁰⁾ This can be seen by comparing a near- E_F valence band at 45 K of Al_{70.5}Pd₂₁Re_{8.5} with that of Ag evaporated onto the alloy (Fig. 9). There is also evidence from the perfect fits of the spectra of this alloy measured at 45 and 9 K (Fig. 9). It may be thus concluded that the Al_{70.5}Pd₂₁Re_{8.5} I alloy, in spite of its high ρ , is metallic down to the temperature of measurement (9 K). However, the observed finite DOS at E_F (Fig. 9) is not incompatible with the I Al-Pd-Re alloy being on the insulating side of the Mott-Anderson metal-insulator transition.

3.2 Pseudogap in decagonal quasicrystals

The low-temperature He II valence band of the D Al₆₅Co₁₅Cu₂₀ alloy measured with an energy resolution of ~ 30 meV exhibits two features (Fig. 10). As shown with the resonance PES technique,⁷¹⁾ the feature close to E_F is predominantly due to states of Co $3d$ character and the feature at $E_B \approx -4.2$ eV is mainly due to the Cu $3d$ -derived states. The partial Co $3d$ and Cu $3d$ states derived from the resonance PES spectra⁷¹⁾ extend to E_F , which means that the DOS(E_F) is dominated by the Co $3d$ - and Cu $3d$ -like states. The decrease of the spectral intensity towards E_F in the valence band of D Al₆₅Co₁₅Cu₂₀ (Fig. 10) was interpreted, using eq. (1) for a positive slope of the normal DOS evaluated from the linear fit of the band in the E_B range from -2.0 to -1.5 eV, as indicative of the presence of the pseudogap.⁵²⁾ However, the analysis based on choosing the normal DOS for the E_B range closer to E_F (the normal DOS with a negative slope) results in no pseudogap. A comparison between the room-temperature PES valence band of the D Al₆₅Co₁₅Cu₂₀ alloy⁷¹⁾ measured at $h\nu = 100$ eV with an energy resolution of 400 meV with the PES spectra calculated²⁸⁾ for different structural models of the D Al-Co-Cu phase shows (Fig. 11) a good agreement for a particular model B2Cu. For all these models, there is no minimum in the DOS at E_F .²⁸⁾ A relatively good agreement between the measured valence band and the calculated one (Fig. 11) was taken²⁸⁾ as evidence for the absence of the pseudogap in the D Al-Co-Cu alloys. Clearly, further high-resolution spectroscopic data probing the unoc-

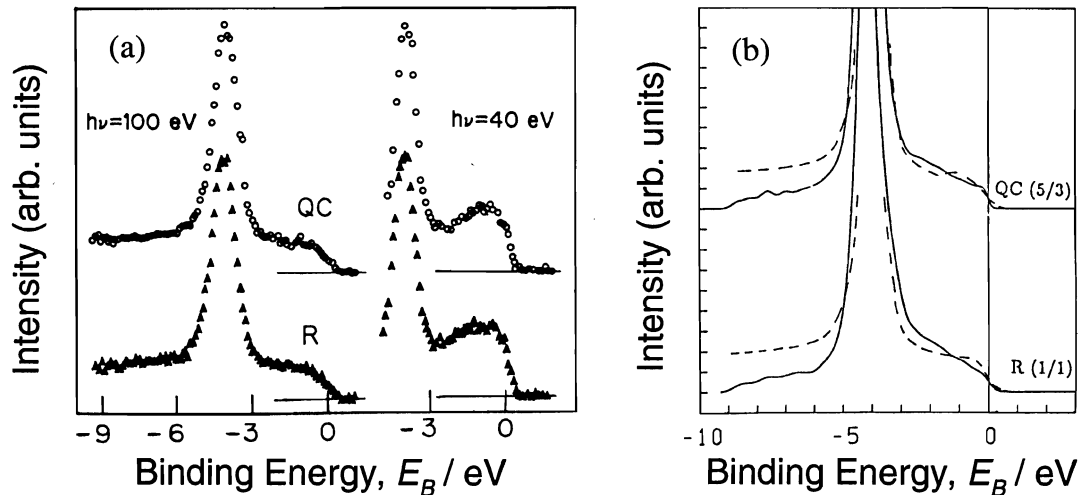


Fig. 7 (a) Room temperature valence bands of I $\text{Al}_{55}\text{Li}_{35.8}\text{Cu}_{9.2}$ and R phase $\text{Al}_{54}\text{Li}_{36.8}\text{Cu}_{9.2}$ measured at $h\nu = 100$ eV with an energy resolution of 700 meV and at $h\nu = 40$ eV with an energy resolution of 400 meV.⁶⁴⁾ (b) Comparison between the $h\nu = 100$ eV valence bands of I $\text{Al}_{55}\text{Li}_{35.8}\text{Cu}_{9.2}$ and R phase $\text{Al}_{54}\text{Li}_{36.8}\text{Cu}_{9.2}$ (broken lines) from (a) with the calculated PES spectra for a 5/3 approximant and R phase (solid line).¹⁵⁾

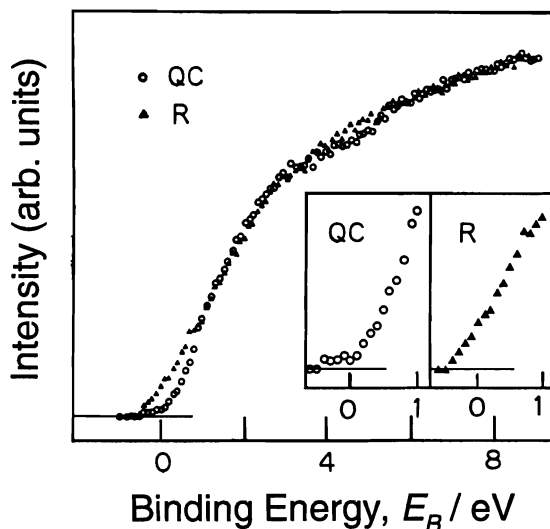


Fig. 8 Room-temperature IPES spectra of I $\text{Al}_{55}\text{Li}_{35.8}\text{Cu}_{9.2}$ and R phase $\text{Al}_{54}\text{Li}_{36.8}\text{Cu}_{9.2}$ measured with an energy resolution of 700 meV. The relative intensities have been normalized at the high binding energy region. The inset shows the spectra close to E_F .⁶⁴⁾

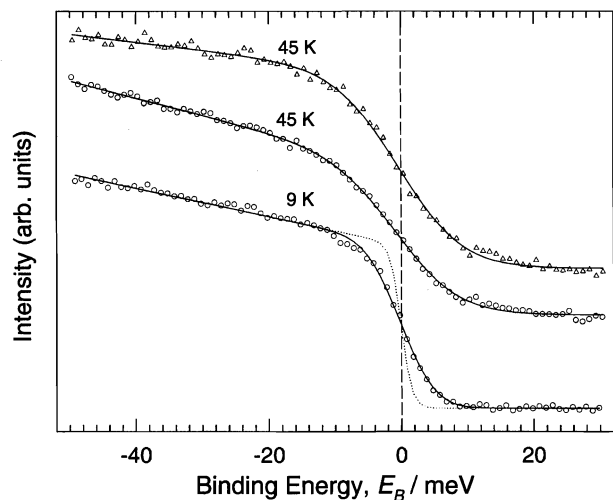


Fig. 9 Near- E_F He I valence band of I $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ (circles) and Ag (triangles) evaporated on it. The solid lines are the fits to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 45 and 9 K (broken curve) and convoluted with a Gaussian whose FWHM is 6.0(5) meV for the 9 K and 9.2(3) meV for the 45 K bands.⁷⁰⁾

occupied DOS are needed to unambiguously determine the presence or absence of the pseudogap in the D Al–Co–Cu system.

The low-temperature He II valence band of the D $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ alloy measured with an energy resolution of ~ 30 meV (Fig. 10) exhibits one strong feature at $E_B \approx -1.4$ eV resulting from the overlap of the Co and Ni 3d-like states.⁷¹⁾ The closeness of these states to E_F results in the high $\text{DOS}(E_F)$. The decrease of the spectral intensity towards E_F in the valence band of D $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ (Fig. 10) was interpreted, using eq. (1) for a positive slope of the normal DOS evaluated from the linear fit of the band in the E_B range from -2.2 to -1.8 eV, as indicative of the presence of the pseudogap.⁵²⁾ However, the analysis based on choosing the normal DOS for the E_B range closer to E_F (the normal DOS with a negative slope) results in no pseudogap. The low-temperature valence band of D $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ was compared with the PES spectrum calculated³¹⁾ for various

structural models of the D Al–Ni–Co system. A reasonable agreement was obtained for a particular structural model V46 (Fig. 12) for which there is no pseudogap in the $\text{DOS}(E_F)$. However, a combination of the room-temperature PES and IPES spectra measured on the single-grain D $\text{Al}_{72}\text{Co}_{16}\text{Ni}_{12}$ alloy shows (Fig. 13) the presence of the pseudogap of the width of ~ 1.7 eV.⁷²⁾ The IPES measurement⁷²⁾ suffers from a poor energy resolution (0.9–1.6 eV) which might affect the location of the IPES band edge on the E_B energy scale.

It can be concluded that the interpretation of the currently available PES/IPES data on the D QCs with regard to the pseudogap is contradictory. Further spectroscopic experiments are required to settle the problem of the possible existence of the pseudogap in D alloys.

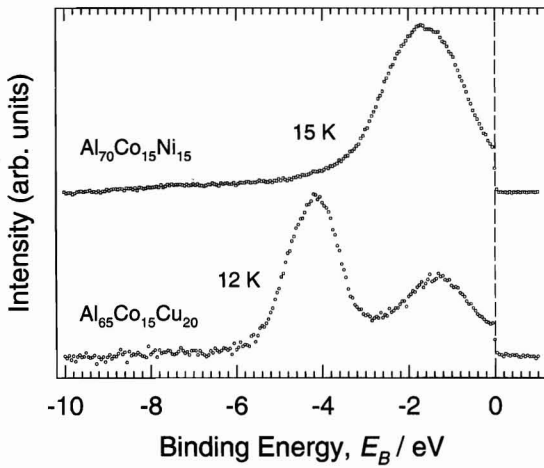


Fig. 10 Low-temperature He II valence bands of the D $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ and $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ alloys measured with an energy resolution of ~ 30 meV.⁵²⁾ The spectra have been normalized to give a constant height between the maximum and minimum count.

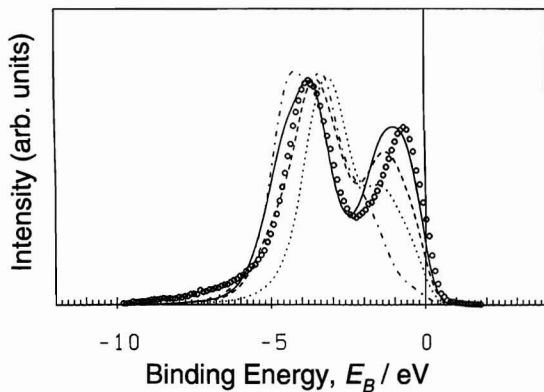


Fig. 11 Comparison of the room-temperature valence band of the D $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ alloy⁷¹⁾ measured at $h\nu = 100$ eV with an energy resolution of 400 meV (open circles) with the PES spectra calculated²⁸⁾ for the structural models B1 (dot-dashed line), B2 (dashed line), B2Cu (full line), and B2Co (dotted line).

3.3 Fine structure of the density of states of quasicrystals

The theoretically predicted spikiness of the DOS in QCs has been claimed to be consistent with the variations of various physical parameters which probe the DOS indirectly. The observation of the variation of γ with composition by a factor of two in the I Al–Cu–Ru alloys was attributed to the rapid variation of DOS.⁷³⁾ The temperature dependencies of the Hall coefficient R_H and of the thermoelectric power S were claimed to require the rapidly varying DOS over the energy scale of ~ 20 meV.^{32,74)} The nonlinear temperature dependence of the Knight shift K and the spin-lattice relaxation rate $1/T_1$ found in the ^{27}Al and ^{63}Cu NMR studies of I Al–Cu–Fe, Al–Cu–Ru and Al–Pd–Mn alloys was argued to be indicative of a sharp feature of the width ~ 20 meV in the $\text{DOS}(E_F)$.⁷⁵⁾ The change of $1/T_1$ by a factor of two upon a hydrogen-to-metal ratio found in the ^1H NMR study of the I $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}\text{H}_x$ alloy was estimated to result from the 40% change of the DOS over an energy range of 75 meV.⁷⁶⁾ The analysis of the temperature dependence of $1/T_1$ determined in the ^{27}Al NMR study of the I $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ alloy concluded that a sharp feature with the $\text{FWHM} = 14$ meV and located at 11 meV above E_F is present in the DOS of this alloy.³⁹⁾ Other

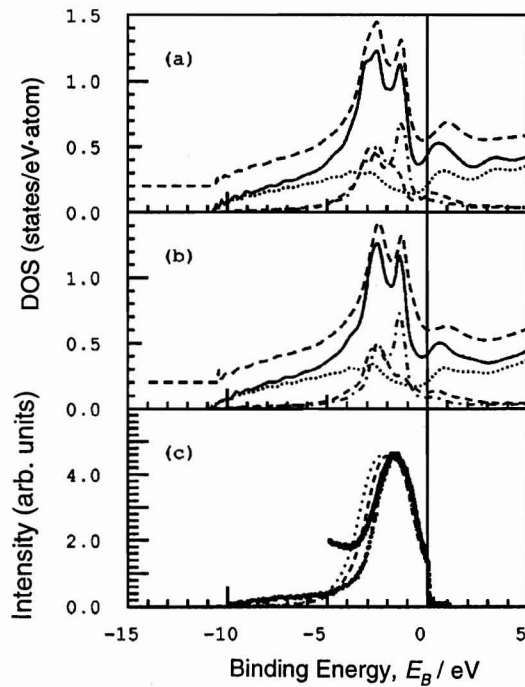


Fig. 12 Total and partial DOS for the 1276-atom structural models V42 (a) and V46 (b) of the D Al–Ni–Co system.³¹⁾ Total DOS–full line; Al DOS–dotted line; Ni DOS–chain line; Co DOS–dashed line. The shifted dashed lines represent the total DOS of the corresponding 484-atom model. (c) Comparison of the low-temperature valence bands of the D $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ alloy from Fig. 10 (full circles) and Ref. 52) (squares) with the PES spectra calculated³¹⁾ for the structural models V42 (dotted line) and V46 (dashed line).

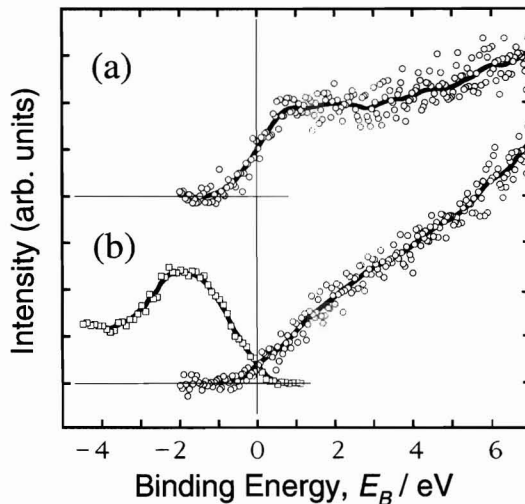


Fig. 13 (a) Room-temperature IPES spectrum of Au. (b) Room-temperature PES and IPES spectra of the single-grain D $\text{Al}_{72}\text{Co}_{16}\text{Ni}_{12}$.⁷²⁾ The solid lines are the smoothed experimental data.

experiments were interpreted against the presence of the DOS spikiness. The lack of dependence of $1/T_1$ upon composition determined in the ^{27}Al NMR study of I Al–Cu–Ru alloys was taken as evidence against the fine structure of the DOS on the energy scale of ~ 20 meV.⁷⁷⁾ The absence of the pressure dependence of $1/T_1$ and K found in the ^{27}Al and ^{63}Cu NMR study of the I $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ alloy was argued to be inconsistent with the DOS fine structure on the energy scale of 10 meV.⁷⁸⁾ The coefficient A of the T^2 contribution to the magnetic susceptibility⁷⁹⁾ and the coefficient β of the T^3 term

of the electronic contribution to the specific heat⁸⁰⁾ are a function of the first and second derivative of $DOS(E_F)$. Large values of these derivatives are expected for a spiky DOS, which would lead to large values of A and β ; this has not been observed experimentally.^{79,80)} The universal relation $\rho \sim \gamma^{-1/2}$ found^{34,35)} for I alloys was interpreted by Mizutani³⁴⁾ as evidence for the smooth DOS at E_F : had the DOS been spiky, such a universal relation would have not existed. The analysis of the temperature dependence of $1/T_1$ determined in the ²⁷Al NMR study of I Al–Cu–Fe and Al–Pd–Mn alloys concluded that there are no sharp features in the DOS of these alloys.³⁹⁾

The predicted DOS spikiness should be detected with the spectroscopic techniques which measure the DOS directly. Experiments carried out with tunneling spectroscopy (TS) technique, which has the energy resolution of $\sim k_B T$ (better than 1 meV at 4.2 K), detected at liquid helium temperatures one sharp feature, located at E_F , of the width ~ 50 – 60 meV in the I Al–Cu–Fe, Al–Pd–Mn and Al–Pd–Re alloys.^{81–84)} However, in another TS study,⁸⁵⁾ this feature was found to be much narrower (~ 20 meV) in the I Al–Cu–Fe and Al–Pd–Mn alloys, but very wide (~ 100 meV) in the Al–Pd–Re alloys. No other spikes could be observed in the tunneling spectra of I alloys.^{81–85)} In a TS experiment carried out on the single-grain D Al₇₃Co₁₀Ni₁₇ alloy the detection of the rich fine structure of the DOS was reported.⁸⁶⁾ This, however, was disputed and was shown to result from Andreev processes.^{87,88)}

To make a meaningful comparison between the measured DOS and the calculated one, the latter must be modified to account for the finite energy resolution of an experiment, the lifetime broadening effects inherent to a given spectroscopic technique used to measure the DOS, and the sample temperature.^{52,62)} It is clear⁵²⁾ that the possible DOS spikiness can be observed at room and/or low temperatures with the PES/IPES techniques with an energy resolution better than ~ 100 meV, and only in the vicinity of E_F . However, such spikes are clearly not observed in the UPS valence bands of polyquasicrystalline and single-grain QCs measured with high [Figs. 2(a), 5(b) and 10] and very high [Figs. 2(b) and 9] energy resolution.^{52,58,61,63,70,89–91)} It must be then concluded that the high-resolution PES results cannot confirm the reality of the predicted spikiness of the DOS in QCs.

Different reasons were invoked in order to explain the failure of the high resolution PES and TS experiments to detect the DOS spikiness. These include the quality of the surface used for these experiments or the presence of disorder even in QCs of the best structural quality (as evidenced by the presence of diffuse scattering).^{52,58)} Recent theoretical studies show that the DOS spikiness predicted in numerous electronic structure calculations^{9–24,26–31)} is an artifact of the calculations.^{25,92)} This would explain why it cannot be detected.

4. Summary

The low-temperature valence band of the single-grain I alloy I Al₇₀Pd_{21.5}Mn_{8.5} has been measured with the high and very high energy resolution UPS technique. The alloy has a clearly developed Fermi edge, and is therefore metallic. The decrease of the spectral intensity toward E_F has been shown to be compatible with the presence of the theoretically predicted pseudogap in the DOS around E_F . The presence of the

theoretically predicted fine structure of the DOS has not been observed even with a resolution of 8.6 meV. A review of the published PES and IPES experimental data on the electronic structure of QCs has also been presented. It has been shown that the data confirms the existence of the pseudogap in the $DOS(E_F)$ in all studied I QCs, but that there is no consensus on its presence in D QCs. It has been suggested that the failure to detect the predicted DOS spikiness in QCs results from the fact that this spikiness is an artifact of electronic structure calculations and, in fact, does not exist.

Acknowledgment

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- 1) *Physical Properties of Quasicrystals*, ed. by Z. M. Stadnik, (Springer-Verlag, Berlin, 1999) pp. 1–438.
- 2) A. P. Smith and N. W. Ashcroft: *Phys. Rev. Lett.* **59** (1987) 1365–1368.
- 3) J. Friedel and F. Dénoyer: *C. R. Acad. Sci. (Paris)* **305** (1987) 171–174.
- 4) V. G. Vaks, V. V. Kamyshenko and G. D. Samolyuk: *Phys. Lett. A* **132** (1988) 131–136.
- 5) J. Friedel: *Helv. Phys. Acta* **61** (1988) 538–556.
- 6) J. Friedel: *Philos. Mag.* **B 65** (1992) 1125–1129.
- 7) M. A. Fradkin: *J. Phys. Condens. Matter* **4** (1992) 10497–10502.
- 8) A. E. Carlsson: *Phys. Rev. B* **47** (1993) 2515–2521.
- 9) T. Fujiwara: *Phys. Rev. B* **40** (1989) 942–946.
- 10) T. Fujiwara and T. Yokokawa: *Phys. Rev. Lett.* **66** (1991) 333–336.
- 11) J. Hafner and M. Krajčič: *Phys. Rev. Lett.* **68** (1992) 2321–2324.
- 12) J. Hafner and M. Krajčič: *Europhys. Lett.* **17** (1992) 145–150.
- 13) J. Hafner and M. Krajčič: *Phys. Rev. B* **47** (1993) 11795–11809.
- 14) G. Trambly de Laissardière and T. Fujiwara: *Phys. Rev. B* **50** (1994) 5999–6005.
- 15) M. Windisch, M. Krajčič and J. Hafner: *J. Phys. Condens. Matter* **6** (1994) 6977–6995.
- 16) M. Krajčič and J. Hafner: *Europhys. Lett.* **27** (1994) 147–152.
- 17) M. Krajčič, M. Windisch, J. Hafner, G. Kresse and M. Mihalkovič: *Phys. Rev. B* **51** (1995) 17355–17378.
- 18) G. Trambly de Laissardière, D. Nguyen Manh, L. Magaud, J. P. Julien, F. Cyrot-Lackmann and D. Mayou: *Phys. Rev. B* **52** (1995) 7920–7933.
- 19) R. G. Hennig and H. Teichler: *Philos. Mag.* **A 76** (1997) 1053–1064.
- 20) G. Dell’Acqua, M. Krajčič and J. Hafner: *J. Phys. Condens. Matter* **9** (1997) 10725–10738.
- 21) S. Roche and T. Fujiwara: *Phys. Rev. B* **58** (1998) 11338–11344.
- 22) M. Krajčič and J. Hafner: *Phys. Rev. B* **59** (1999) 8347–8350.
- 23) M. Krajčič and J. Hafner: *J. Phys. Condens. Matter* **12** (2000) 5831–5842.
- 24) G. Trambly de Laissardière and T. Fujiwara: *Phys. Rev. B* **50** (1994) 9843–9850.
- 25) R. Haerle and P. Kramer: *Phys. Rev. B* **58** (1998) 716–720.
- 26) R. F. Sabiryanov and S. K. Bose: *J. Phys. Condens. Matter* **6** (1994) 6197–6210; erratum **7** (1996) 2375.
- 27) R. F. Sabiryanov, S. K. Bose and S. E. Burkov: *J. Phys. Condens. Matter* **7** (1995) 5437–5459.
- 28) M. Krajčič, J. Hafner and M. Mihalkovič: *Phys. Rev. B* **56** (1997) 3072–3085.
- 29) M. Krajčič, J. Hafner and M. Mihalkovič: *Europhys. Lett.* **34** (1996) 207–212.
- 30) M. Krajčič, J. Hafner and M. Mihalkovič: *Phys. Rev. B* **55** (1997) 843–855.
- 31) M. Krajčič, J. Hafner and M. Mihalkovič: *Phys. Rev. B* **62** (2000) 243–255.
- 32) S. J. Poon: *Adv. Phys.* **41** (1992) 303–363.
- 33) K. Kimura and S. Takeuchi: *Quasicrystals, The State of the Art*, ed. D. P. DiVincenzo and P. J. Steinhardt, (World Scientific, Singapore, 1999) pp. 325–359.
- 34) U. Mizutani: *J. Phys. Condens. Matter* **10** (1998) 4609–4623.
- 35) Ö. Rapp: *Physical Properties of Quasicrystals*, ed. by Z. M. Stadnik, (Springer-Verlag, Berlin, 1999) pp. 127–167.

- 36) F. Hippert, L. Kandel, Y. Calvayrac and B. Dubost: *Phys. Rev. Lett.* **69** (1992) 2086–2089.
- 37) E. A. Hill, T. C. Chang, Y. Wu, S. J. Poon, F. S. Pierce and Z. M. Stadnik: *Phys. Rev. B* **49** (1994) 8615–8620.
- 38) A. Shastri, F. Borsa, D. R. Torgeson, J. E. Shield and A. I. Goldman: *Phys. Rev. B* **50** (1994) 15651–15667.
- 39) J. Dolinšek, M. Klanjšek, T. Apih, A. Smontara, J. C. Lasjaunias, J. M. Dubois and S. J. Poon: *Phys. Rev. B* **62** (2000) 8862–8870.
- 40) S. E. Burkov, T. Timusk and N. W. Ashcroft: *J. Phys. Condens. Matter* **4** (1992) 9447–9458.
- 41) X. Wu, C. C. Homes, S. E. Burkov, T. Timusk, F. S. Pierce, S. J. Poon, S. L. Cooper and M. A. Karlow: *J. Phys. Condens. Matter* **5** (1993) 5975–5990.
- 42) D. Macko and M. Kašpárková: *Philos. Mag. Lett.* **67** (1993) 307–312.
- 43) L. Degiorgi, M. A. Chernikov, C. Beeli and H. R. Ott: *Solid State Commun.* **87** (1993) 721–726.
- 44) D. N. Basov, F. S. Pierce, P. Volkov, S. J. Poon and T. Timusk: *Phys. Rev. Lett.* **73** (1994) 1865–1868.
- 45) A. D. Bianchi, F. Bommeli, M. A. Chernikov, U. Gubler, L. Degiorgi and H. R. Ott: *Phys. Rev. B* **55** (1997) 5730–5735.
- 46) M. Takeda, R. Tamura, Y. Sakairi and K. Kimura: *J. Phys. Soc. Jpn.* **66** (1997) 1924–1927.
- 47) Wang Yun-ping, Zhang Dian-lin and L. F. Chen: *Phys. Rev. B* **48** (1993) 10542–10545.
- 48) R. Lüch and S. Kek: *J. Non-Cryst. Solids* **153–154** (1993) 329–333.
- 49) K. Edagawa, M. A. Chernikov, A. D. Bianchi, E. Felder, U. Gubler and H. R. Ott: *Phys. Rev. Lett.* **77** (1996) 1071–1074.
- 50) A. D. Bianchi, F. Bommeli, E. Felder, M. Kenzelmann, M. A. Chernikov, L. Degiorgi, H. R. Ott and K. Edagawa: *Phys. Rev. B* **58** (1998) 3046–3056.
- 51) D. N. Basov, T. Timusk, F. Barakat, J. Greedan and B. Grushko: *Phys. Rev. Lett.* **72** (1994) 1937–1940.
- 52) Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa, S. Takeuchi and K. H. J. Buschow: *Phys. Rev. B* **55** (1997) 10938–10951.
- 53) Z. M. Stadnik, D. Purdie, Y. Baer and T. A. Lograsso, unpublished.
- 54) C. J. Jenks, D. W. Delaney, T. E. Bloomer, S.-L. Chang, T. A. Lograsso, Z. Shen, C.-M. Zhang and P. A. Thiel: *Appl. Surf. Sci.* **103** (1996) 485–493.
- 55) Z. Shen, M. J. Kramer, C. J. Jenks, A. I. Goldman, T. Lograsso, D. Delaney, M. Heinzig, W. Raberg and P. A. Thiel: *Phys. Rev. B* **58** (1998) 9961–9971.
- 56) M. Grioni, D. Malterre and Y. Baer: *J. Low Temp. Phys.* **99** (1995) 195–200.
- 57) G. W. Zhang, Z. M. Stadnik, A.-P. Tsai, A. Inoue and T. Miyazaki: *Z. Phys. B* **97** (1995) 439–452.
- 58) Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa and S. Takeuchi: *Phys. Rev. Lett.* **77** (1996) 1777–1780.
- 59) G. W. Zhang, Z. M. Stadnik, A.-P. Tsai and A. Inoue: *Phys. Rev. B* **50** (1994) 6696–6708.
- 60) G. W. Zhang and Z. M. Stadnik: *Proc. 5th Int. Conf. Quasicrystals*, ed. by Ch. Janot and R. Mosseri, (World Scientific, Singapore, 1995) pp. 552–555.
- 61) M. Mori, S. Matsuo, T. Ishimasa, T. Matsuura, K. Kamiya, H. Inokuchi and T. Matsukawa: *J. Phys. Condens. Matter* **3** (1991) 767–771.
- 62) S. Hüfner: *Photoelectron Spectroscopy*, (Springer-Verlag, Berlin, 1996).
- 63) G. Neuhold, S. R. Barman, K. Horn, W. Theis, P. Ebert and K. Urban: *Phys. Rev. B* **58** (1998) 734–738.
- 64) H. Matsubara, S. Ogawa, T. Kinoshita, K. Kishi, S. Takeuchi, K. Kimura and S. Suga: *Jpn. J. Appl. Phys. A* **30** (1991) L389–L392.
- 65) M. Rodmar, F. Zavaliche, S. Poon and Ö. Rapp: *Phys. Rev. B* **60** (1999) 10807–10810.
- 66) C.-R. Wang and S.-T. Lin: *J. Phys. Soc. Jpn.* **68** (1999) 3988–3993.
- 67) M. Rodmar, M. Ahlgre, D. Oberschmidt, C. Gignoux, J. Delahaye, C. Berger, S. Poon and Ö. Rapp: *Phys. Rev. B* **61** (2000) 3936–3950.
- 68) J. J. Préjean, J. C. Lasjaunias, C. Berger and A. Sulpice: *Phys. Rev. B* **61** (2000) 9356–9364.
- 69) R. Rosenbaum, R. Haberken, P. Häussler, E. Palm, T. Murphy, S. Hannahs and B. Brand: *J. Phys. Condens. Matter* **12** (2000) 9735–9749.
- 70) Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa and S. Takeuchi: *Proc. 6th Int. Conf. Quasicrystals*, ed. by S. Takeuchi and T. Fujiwara, (World Scientific, Singapore, 1998) pp. 563–570.
- 71) Z. M. Stadnik, G. W. Zhang, A.-P. Tsai and A. Inoue: *Phys. Rev. B* **51** (1995) 11358–11368.
- 72) K. Soda, K. Nozawa, Y. Yanagida, K. Morita, U. Mizutani, Y. Yokoyama, R. Note, A. Inoue, H. Ishii, Y. Tezuka and S. Shin: *J. Electron Spectrosc. Relat. Phenom.* **88–91** (1998) 415–418.
- 73) B. D. Biggs, S. J. Poon and N. R. Munirathnam: *Phys. Rev. Lett.* **65** (1990) 2700–2703.
- 74) B. D. Biggs, Y. Li and S. J. Poon: *Phys. Rev. B* **43** (1991) 8747–8750.
- 75) X.-P. Tang, E. A. Hill, S. K. Wonnell, S. J. Poon and Y. Wu: *Phys. Rev. Lett.* **79** (1997) 1070–1073.
- 76) N. A. Stojanovich, D. W. Pfitsch, A. F. McDowell, E. H. Majzoub, J. Y. Kim and K. F. Kelton: *Philos. Mag. Lett.* **80** (2000) 763–776.
- 77) A. Shastri, F. Borsa, D. R. Torgeson, J. E. Shield and A. I. Goldman: *Phys. Rev. B* **50** (1994) 15651–15667.
- 78) A. Shastri, D. B. Baker, M. S. Conradi, F. Borsa and D. R. Torgeson: *Phys. Rev. B* **52** (1995) 12681–12684.
- 79) A. Kobayashi, S. Matsuo, T. Ishimasa and H. Nakano: *J. Phys. Condens. Matter* **9** (1997) 3205–3217.
- 80) Ch. Wälti, E. Felder, M. A. Chernikov, H. R. Ott, M. de Boissieu and C. Janot: *Phys. Rev. B* **57** (1998) 10504–10511.
- 81) T. Klein, O. G. Symko, D. N. Davydov and A. G. M. Jansen: *Phys. Rev. Lett.* **74** (1995) 3656–3659.
- 82) D. N. Davydov, D. Mayou, C. Berger, C. Gignoux, A. Neumann, A. G. M. Jansen and P. Wyder: *Phys. Rev. Lett.* **77** (1996) 3173–3176.
- 83) T. Schaub, J. Delahaye, C. Gignoux, C. Berger, G. Fourcaudot, F. Giroud, T. Grenet and A. G. M. Jansen: *J. Non-Cryst. Solids* **250–252** (1999) 874–877.
- 84) J. Delahaye, C. Gignoux, T. Schaub, C. Berger, T. Grenet, A. Sulpice, J. J. Préjean and J. C. Lasjaunias: *J. Non-Cryst. Solids* **250–252** (1999) 878–882.
- 85) R. Escudero, J. C. Lasjaunias, Y. Calvayrac and M. Boudard: *J. Phys. Condens. Matter* **11** (1999) 383–404.
- 86) Li Guohong, He Haifeng, Wang Yunping, Lu Li, Li Shanlin, Jing Xiunian and Zhang Dianlin: *Phys. Rev. Lett.* **82** (1999) 1229–1232.
- 87) C. Berger, D. Mayou, T. Grenet and Z. Ovadyahu: *Phys. Rev. Lett.* **83** (1999) 3968.
- 88) Li Guohong, He Haifeng, Wang Yunping, Lu Li, Li Shanlin, Jing Xiunian and Zhang Dianlin: *Phys. Rev. Lett.* **83** (1999) 3969.
- 89) X. Wu, S. W. Kycia, C. G. Olson, P. J. Benning, A. I. Goldman and D. W. Lynch: *Phys. Rev. Lett.* **75** (1995) 4540–4543.
- 90) D. Naumović, P. Aebi, L. Schlapbach, C. Beeli, T. A. Lograsso and D. W. Delaney: *Phys. Rev. B* **60** (1999) R16330–R16333.
- 91) E. Rotenberg, W. Theis, K. Horn and P. Gille: *Nature* **406** (2000) 602–605.
- 92) E. S. Zijlstra and T. Janssen: *Europhys. Lett.* **52** (2000) 578–583.