Electronic Structure of Quasicrystals

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The results of low-temperature, ultrahigh-energy-resolution ultra-violet photoelectron spectroscopy studies of the electronic structure of quasicrystals are reviewed.

Quasicrystals (QCs) are a new form of matter 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 symmetry axes [1]. A central problem in condensed-matter physics is to determine whether quasiperiodicity leads to physical properties which are significantly different from those of crystalline and amorphous materials.

The physical properties of QCs are very unusual [1]. Here we discuss the electronic structure of QCs as studied by low-temperature, ultrahigh-energy-resolution ultraviolet photoelectron spectroscopy (UPS) [2]. There are two major theoretical predictions of the electronic structure of QCs [3]. First, for the compositions at which the QCs form, the Fermi surface-effective Brillouin zone interaction results in the minimum of the electronic density of states (DOS) at the Fermi level (E_F). This means that a Hume-Rothery-type electronic mechanism is mainly responsible for the stabilization of QCs. Second, the DOS of QCs is very unusual in that it consists of many very fine spiked peaks with widths of about 10 meV. This spikiness is believed to be responsible for the observed unusual sensitivity of the electrical conductivity of QCs to slight changes in their composition. 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 structure-induced pseudogap does occur in both crystalline and amorphous systems. However, the predicted DOS spikiness seems to be such a unique property which distinguishes QCs from other materials.

The low-temperature UPS He II ($h\nu = 40.8$ eV) valence bands of the icosahedral (*i*) series Al-Cu-Mn (TM=Fe,Ru,Os) have a two-peak structure (Fig. 1). The feature at the binding energy (BE) of about -4.1 eV is mainly due to the Cu $3d$-derived states. The resonant and the Cooper minimum photoelectron experiments, together with the photoelectron experiments carried out in the constant-initial-state mode, have established [4,5] that the broad feature close to E_F is predominantly due to the states of Fe $3d$, Ru $4d$, and Os $5d$ character, as appropriate. The positions and intensities of the Cu and Fe $3d$ features in the valence band of *i*-Al-Cu-Fe (Fig. 1) agree relatively well with those obtained from the theoretical DOS (Fig. 2) appropriately broadened to account for the lifetime broadening effects inherent to the UPS technique and the finite energy resolution of an UPS experiment [2].
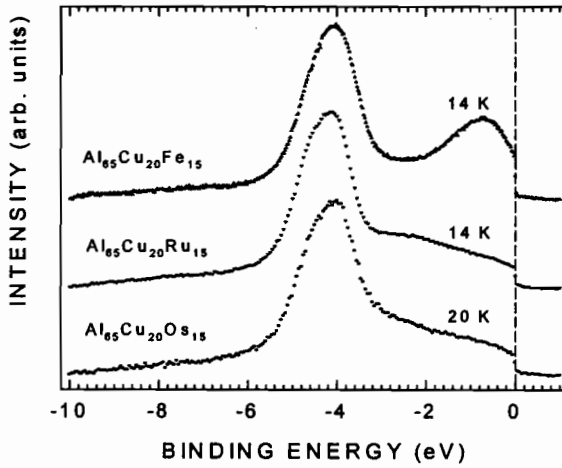
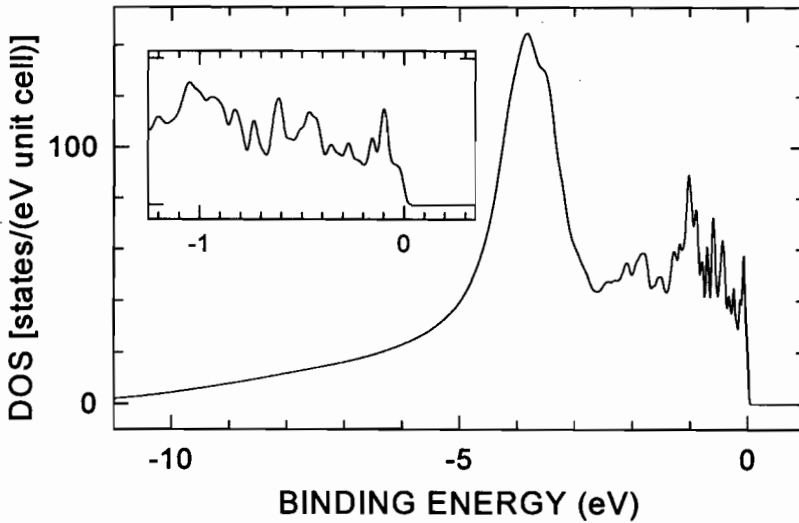Fig. 1. Low-temperature He II valence bands of i QCs $Al_{65}Cu_{20}TM_{15}$ (TM=Fe,Ru,Os). The energy resolution is about 30 meV.

Fig. 2. Occupied part of the DOS for the 1/1 i approximant $Al_{80}Cu_{32}Fe_{16}$ from Ref. 6 multiplied by the Fermi-Dirac distribution function at 14 K and convoluted with a Lorentzian whose HWHM is $(0.02 \text{ eV}^{-1})BE^2$ and a Gaussian whose FWHM is 31.6 meV [2]. The inset shows the broadened DOS in the vicinity of E_F.

The decrease of the spectral intensity toward E_F, which is clearly distinguishable from the Fermi-edge cutoff [Figs. 3(a) and 3(b)], can be shown to be compatible with the presence of a pseudogap, using a model proposed by Mori *et al.* [4]. As conventional alloys of QC-forming elements do not generally display a DOS minimum close to E_F, the model assumes that a simple linear extrapolation of the spectra for the BE range directly before the peak of the valence band feature close to E_F represents the DOS of an alloy without a pseudogap (the normal DOS). The presence of the pseudogap would result in an intensity dip which is assumed to be of Lorentzian shape. Thus the observed intensity close to E_F is the convolution of the normal DOS multiplied by the pseudogap Lorentzian function and by the Fermi-Dirac distribution function, and the experimental resolution Gaussian function [2,3]. This model [Figs. 3(a') and 3(b')] fits well the near-E_F region of the valence bands of i-$Al_{65}Cu_{20}Fe_{15}$ at 14 and 283 K [Figs. 3(a) and 3(b)] and of other i and decagonal alloys [2]. The high-resolution UPS data are in support for the theoretically predicted presence of the pseudogap in QCs.
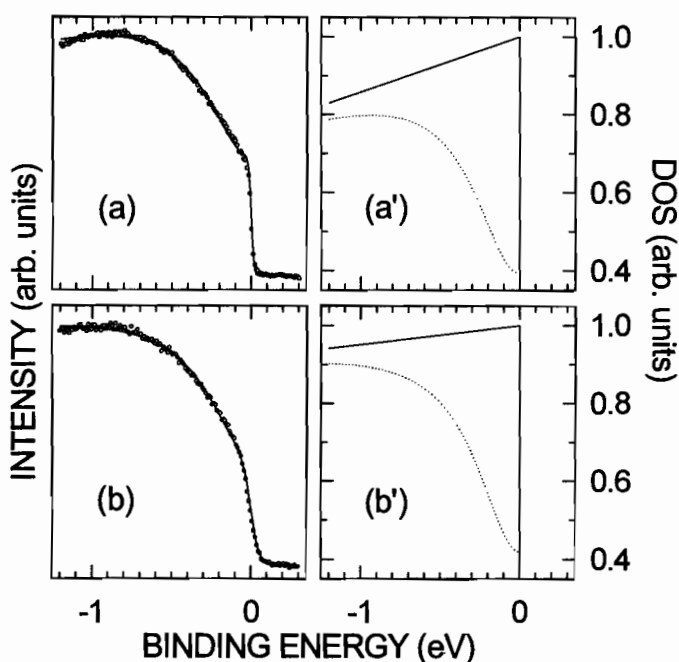

Fig. 3.   He II valence regions close to E_F (open circles) of i-$Al_{65}Cu_{20}Fe_{15}$ measured at (a) 14 K and (b) 283 K with an energy resolution of 31.6(1.8) meV fitted (solid line) to the corresponding model DOS in (a') and (b'). The solid lines in (a') and (b') represent the normal DOS at 0 K and the broken lines show the Lorentzian dip which must be subtracted from the normal DOS in order to fit the valence-band regions in (a) and (b) [2].

In order to assess the predicted existence of the DOS spikiness, a meaningful comparison between the measured DOS spectra and the calculated DOS has to be made. This involves modifying the theoretical DOS to account for the sample temperature, the lifetime broadening effects inherent to the UPS technique, and the finite energy resolution of an UPS spectrometer [2]. Figure 2 shows the occupied part of the theoretical DOS [6] modified in such a way (the chosen temperature of 14 K and the Gaussian full width at half maximum of 31.6 meV correspond to the parameters of the experimental spectrum of i-$Al_{65}Cu_{20}Fe_{15}$ in Fig. 1). It is clear that the predicted DOS spikiness should be observed for BEs up to a few eV below E_F (the fine features of DOS for lower BEs are smeared out by the lifetime broadening effects). Obviously, the DOS spikiness should be observed even more readily for the ultrahigh-energy-resolution (<10 meV). The measured UPS spectra with high- [Figs. 1, 3(a) and 3(b)] and ultrahigh- (Fig. 4) energy resolution show a lack of any fine structure. It must be then concluded that the predicted DOS spikiness is not observed in the UPS spectra measured with the highest-energy resolution presently attainable.
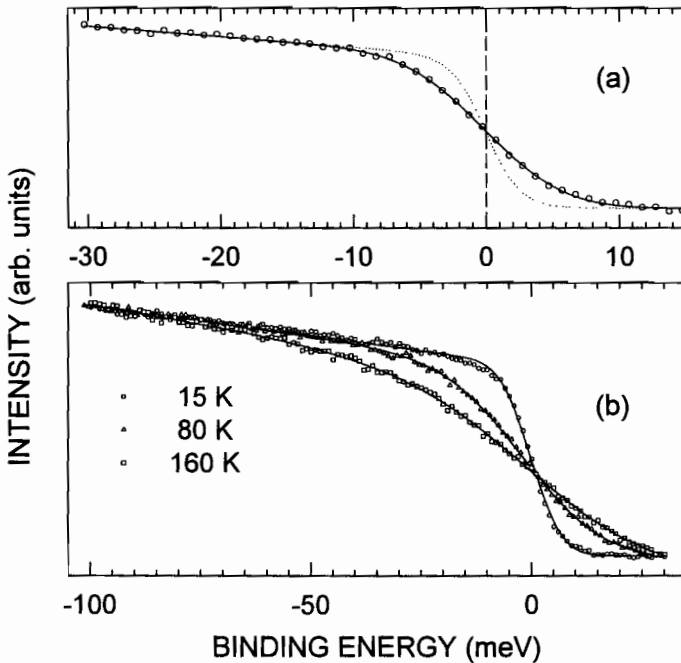

Fig. 4. (a) Near-E_F He I ($h\nu = 21.2$ eV) valence band of i-$Al_{65}Cu_{20}Fe_{15}$ at 13 K. The solid line is a fit to a linearly decreasing intensity multiplied by the Feri-Dirac function at 13 K (broken curve) and convoluted with a Gaussian whose full width at half maximum is equal to 6.2(2) meV. Note that the step between the data points is 1 meV. (b) Near-E_F He I valence band of i-$Al_{65}Cu_{20}Fe_{15}$ measured at different temperatures. The solid lines are the fits as described in (a). Note the different BE scales in (a) and (b).

It may not be possible to detect the predicted DOS spikiness even with the UPS experiments of the highest energy resolution because of the existence of the chemical or topological disorder in QCs of high structural quality. Such disorder, which is not taken into account in the electronic structure calculations, may wash out the DOS spikiness induced by quasiperiodicity [7]. There are some experimental facts which support this suggestion. Diffuse scattering is often observed in x-ray, electron-, and neutron-diffraction patterns of high-quality QCs [1]. Its presence indicates that some disorder must exist in the diffracting structure. Local probes, such as Mössbauer spectroscopy [8], NMR [9], and nuclear quadrupole resonance [9,10], clearly detect the distribution of the electric quadrupole splittings of high-quality QCs. Such a distribution can be detected only if there is a chemical and/or topological disorder in the investigated samples. The apparent success of quantum interference theories, which were originally developed for highly disordered conductors, in accounting for the temperature and field dependencies of the electrical conductivity and magnetoresistance of high-quality QCs [1] also indicates the importance of chemical disorder. And finally, it is conceivable that the predicted DOS spikiness is an artifact of the calculations [11].
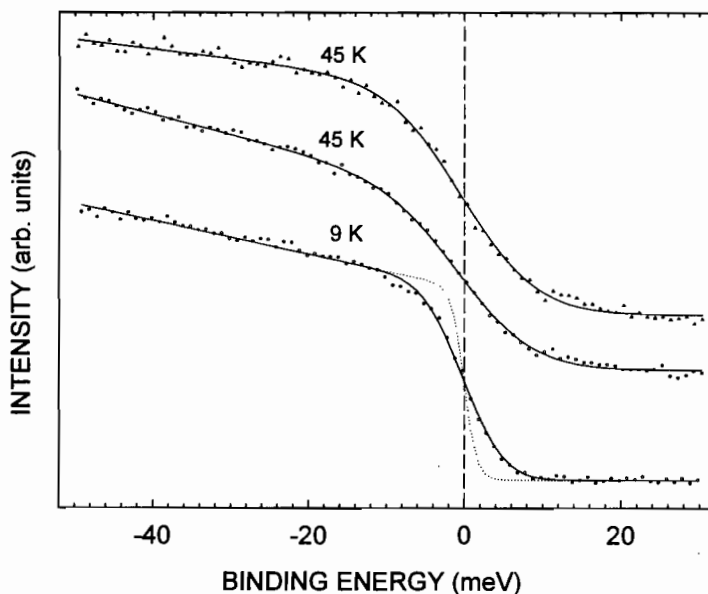

Fig. 5. Near-E_F He I valence band of i-Al$_{70.5}$Pd$_{21}$Re$_{8.5}$ (circles) and Ag (triangles) evaporated on it. The solid lines are the fits to a linearly decreasing intensity multiplied by the Fermi Dirac function at 45 and 9 K (broken curve) and convoluted with a Gaussian whose full width at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

A clear presence of the Fermi edge in the UPS valence bands and its temperature evolution following the Fermi-Dirac function [Figs. 1, 3(a) and 3(b), and 4] shows that QCs, in spite of their very large electrical resistivities [1], are metallic. Even for the *i*-Al-Pd-Re alloys which have the highest values of the electrical resistivities, and which were labeled "insulating" [1], the presence of the Fermi edge (Fig. 5) proves their metallic character.

The electronic structure results discussed above show no unusual features that could be the consequence of the quasiperiodic order. The unexpectedly high value of the electrical resistivity of many *i* alloys, which consist of normal metallic elements, was thought to be indicative of their unique induced by their quasiperiodic structure. However, similarly high values of the electrical resistivities were observed in approximants to QCs [1]. Furthermore, high electrical resistivity and its negative temperature coefficient were also observed in some crystalline alloys consisting of normal metallic elements whose structure is unrelated to the structure of QCs. For example, the Heusler-type Fe_2VAl alloy exhibits a semiconductor-like behavior of the electrical resistivity, yet its valence band clearly shows the presence of the Fermi edge [12]. It has to be concluded that, as yet, no conclusive experimental evidence has been found to support the claim that the distinct physical properties of QCs are due to their quasiperiodic nature and which therefore do not occur in crystalline or amorphous materials. This is perhaps not surprising since there is no sound physical basis to expect that quasiperiodicity should lead to physical properties distinctly different from those found in periodic systems.

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