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

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The results of low-temperature, ultrahigh-energy-resolution ultraviolet photoemission spectroscopy (PES) studies of the electronic structure of stable icosahedral alloys are presented. It is shown that that these alloys have a clearly developed Fermi edge, and are thus metallic down to the temperature of measurement (~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.

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. These low-temperature σ values are significantly smaller than the Mott's "minimum metallic conductivity" of 200 $\Omega^{-1}\text{cm}^{-1}$ for the metal-insulator transition.

The Al-Cu-TM (TM=Fe,Ru,Os) *i* alloys were labelled "marginally metallic" or "semiconducting", whereas the Al-Pd-Re *i* alloys were called "insulators".[2,3] Other unusual physical properties of *i* alloys are reviewed in Ref. 1.

At present there is no well-established theory which would account for the observed unusual physical properties of *i* alloys.[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.[4,5] 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,[1,6] have been recently proposed to explain the unusual transport properties of *i* alloys.

In order to directly and unambiguously determine the metallic or non-metallic character of the *i* alloys and to verify the hypothesis of the pseudogap and the DOS spikiness, PES measurements with ultrahigh energy resolution are essential.[1] 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_BT.[7] In this paper we report the main results of an extensive study of the electronic structure of stable *i* alloys, 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* alloys studied here were prepared as described elsewhere.[1] 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. 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. [7] 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 $\leq$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. [1]

3 Results and Discussion

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

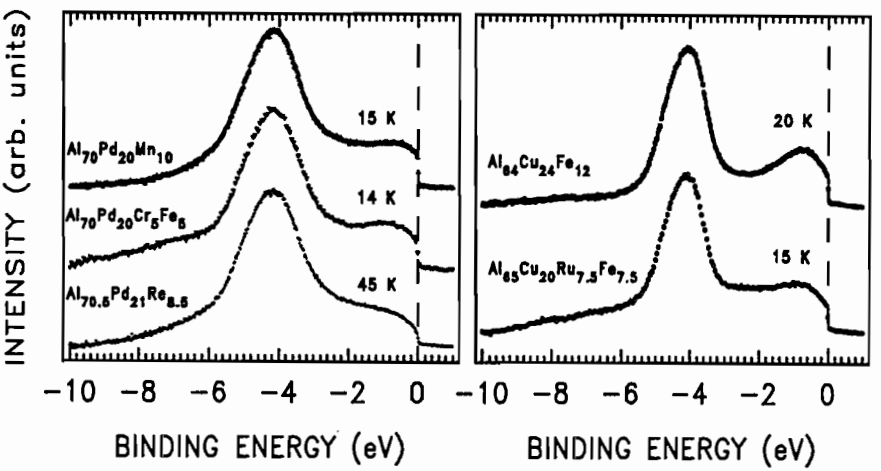

Figure 1: Low-temperature He II valence bands of *i* alloys. The energy resolution is ~30 meV. The spectra have been normalized to give a constant height between the maximum and minimum count.

The valence band region of *i* alloys close to E_F was examined with the highest available energy resolution. [1,8] 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 fitted perfectly 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)]. Additional evidence is also in 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* alloys.[1,8] This constitutes a direct and convincing proof that these *i* alloys, in spite of their unusually low values of σ, are metallic down to the temperature of measurement (9 K).

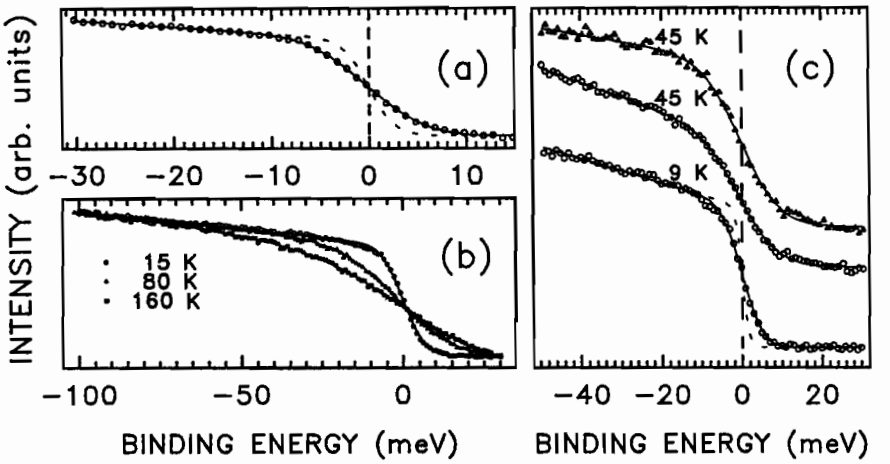

Figure 2: (a) Near-E_F He I valence band of $Al_{65}Cu_{20}Ru_{7.5}Fe_{7.5}$ at 15 K. The solid line is a fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 15 K (broken curve) and convoluted with a Gaussian whose FWHM is equal to 9.8(2) meV. Note that the step between the 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.

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 and 2). As we show elsewhere, [1,8] this spectral intensity decrease is compatible with the presence of the theoretically predicted pseudogap in the DOS around E_F.

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- (Fig. 1) 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) *i* alloys. 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 (Mössbauer spectroscopy, NMR, and nuclear quadrupole resonance) clearly show the presence of distributions of the hyperfine parameters in the structurally perfect *i* alloys. Such distributions can only occur if there is chemical/topological disorder in the samples. [1] Second, diffuse scattering is often observed in X-ray, electron, and neutron diffraction patterns of high-quality poly-quasicrystalline and single-grain *i* alloys. [1] 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.

References

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