PHOTOEMISSION STUDIES OF STABLE, ICOSAHEDRAL ALLOYS

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ABSTRACT

The results of recent synchrotron-radiation-based photoemission spectroscopy studies of the high-quality, stable, icosahedral alloys $Al_{65}Cu_{20}TM_{15}$ (TM=Fe,Ru,Os) and $Al_{70}Pd_{20}Mn_{10}$ are presented. The features due to the d-derived electronic states have been identified in the valence bands and the partial density of states of d character have been extracted. Within the resolution of the experiment, no convincing evidence for the possible existence of a pseudogap at the Fermi level could be found. The need of high-resolution spectroscopic measurements in studies of the electronic structure of icosahedral alloys has been emphasised.

1. Introduction

The stable, icosahedral alloys (IA) of high structural quality exhibit some unusual transport properties.[1] Their most salient feature, which is not expected for alloys formed of normal metallic elements, is the very high value of the electrical resistivity, which locates them at the border of the metal-insulator transition. The temperature coefficient of the resistivity is generally negative, which is inconsistent with the expected behaviour for metals. The resistivity of these IA increases as their structural quality is improved by annealing, in contrast to the behaviour of typical metals. Additionally, the resistivity is very sensitive to sample composition, which is reminiscent of doping effects in semiconductors. Other anomalies in the transport properties involve the very low electronic contribution to the specific heat, the large and strongly temperature-dependent Hall coefficient and thermoelectric power, and a non-Drude-like optical conductivity.[1] From a magnetic point of view, these IA are unusual in that they are diamagnetic in spite of containing significant concentrations of magnetic elements.[1,2]

The properties mentioned above have been interpreted qualitatively[1] using several models, none of which is firmly established yet. By far the most commonly invoked model is based on a Hume-Rothery effect, which implies a Fermi surface-Brillouin zone interaction leading to the opening of a pseudogap

at the Fermi level (E_F). The notion of a structure-induced pseudogap at E_F seems to be supported by a theory based on the electronic structure calculations performed for the lowest-order crystalline approximants.[1-3] The other two mechanisms invoked to explain transport properties of IA are the tunnelling model[4] and the model based on the intraband transition mechanism.[5]

It should be emphasized that the transport measurements mentioned above provide *indirect* information on the density of states (DOS) at one particular energy (E_F). To determine the electronic structure of IA one needs information not only on the DOS(E_F), but also on the DOS below and above E_F. Therefore, studies using spectroscopic techniques which probe DOS *directly* at energies in the vicinity of E_F are very desirable. In this paper we present some recent extensive studies of the electronic structure of quasicrystals using the synchrotron-radiation-based photoemission spectroscopy (PES) technique.

2. Experimental

Ingots of nominal composition $Al_{65}Cu_{20}TM_{10}$ (TM=Fe,Ru,Os) and $Al_{70}Pd_{20}Mn_{10}$ were prepared by melting high-purity source metals in an argon atmosphere using an arc furnace and were annealed in vacuum under appropriate conditions. The x-ray diffraction study showed that the samples are single phase and exhibit resolution-limited Bragg-peak widths.[6]

Photoemission spectra were collected on beamline U14A at the National Synchrotron Light Source at the Brookhaven National Laboratory. The resulting overall resolution was about 0.4 eV. Other experimental details were the same as described elsewhere.[2] The PES spectra presented here were corrected for the energy dependence of the electron transmission of the electron energy analyzer, the time dependent photon flux, and the secondary-electron background.[2] The spectra corrected in such a way can be compared not only with respect to their shape but also in terms of their intensities.

3. Results and Discussion

Different features associated with the d-derived electronic states in a valence band can be determined by performing PES measurements for photon energies, hν, in the resonance or in the Cooper minimum region.[2] As an example, the valence bands of icosahedral $Al_{65}Cu_{20}Os_{15}$ show clearly that the feature at the binding energy BE=-1.5 eV is suppressed at hν=44.5 eV [Fig. 1(a)], which corresponds to the Os 5p→5d transition, and is almost completely quenched at hν=130 eV [Fig. 1(b)], which corresponds to the Cooper minimum in the photoionization cross section, σ, for Os 5d orbitals.[7] Thus, the feature at BE=-1.5 eV is mainly due to the Os 5d-derived states, whereas the feature at BE=-3.7 eV is predominantly of the Cu 3d character. The features due to the Al sp states

cannot be easily identified in the PES valence bands since the σ values corresponding to the Al sp orbitals are very small.[7]

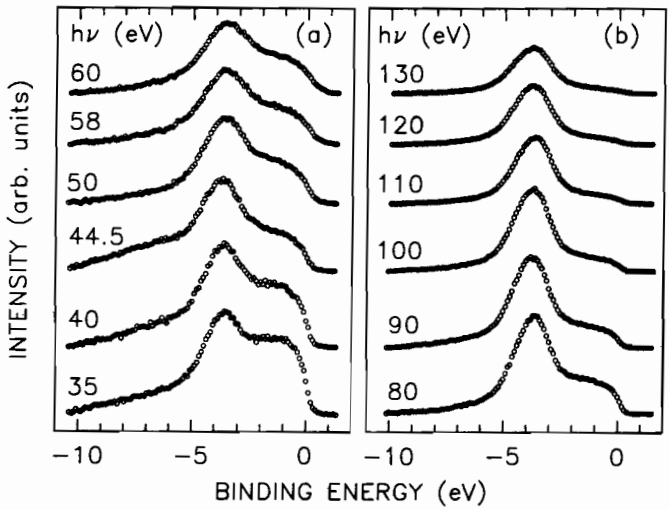

Fig. 1. Valence bands of icosahedral $Al_{65}Cu_{20}Os_{15}$ measured for different photon energies hν around (a) the Os 5p→5d transition and (b) the Os 5d Cooper minimum.

To a first approximation, the measured PES intensity of the studied IA can be represented as a sum of the weighted partial d-like DOS of Cu and TM, or Pd and Mn elements, where the weights correspond to the appropriate σ values.[6] Thus, by measuring valence bands at two photon energies such partial DOS can be extracted (Fig. 2). It is worth mentioning that before the advent of synchrotron-radiation-based PES, such partial DOS could be determined only by using the soft x-ray emission (SXE) technique. The reliability of the derived Os 5d and Cu 3d DOS (Fig. 2) is confirmed by the fact the valence bands measured for other hν values are well reproduced (Fig. 3) using these partial DOS and the corresponding σ values. By using this approach, the partial DOS associated with the d-like elements in the studied IA was determined.[6] These results demonstrate that there is a non-negligible contribution of the Os 5d-, Ru 4d-, Fe 3d-, and Mn 3d-derived states to the DOS(E_F) in the studied IA.

When the valence bands of the studied IA are compared, two common characteristics stand out. Firstly, the Cu 3d- and Pd 4d-derived states are further away from E_F as compared to their locations in the Cu and Pd elements, whereas the features associated the Os 5d, Ru 4d-, Fe and Mn 3d-derived states remain close to E_F. Thus the contribution of the latter to the DOS(E_F), although small, is nevertheless not negligible. Secondly, there is a strong reduction of the PES intensity as the energy approaches E_F. This decrease, which has been also observed in the SXE spectra of IA,[8] has been interpreted as evidence for the

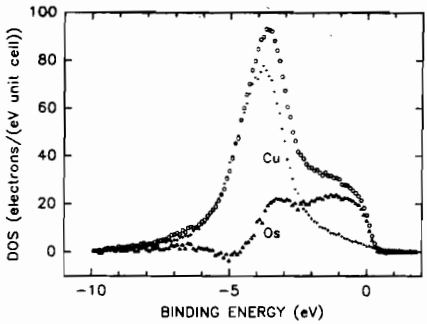

Fig. 2. Partial DOS associated with the Os 5d-derived states (△) and the Cu 3d-derived states (+) obtained from the hν=80 eV and hν=130 eV valence bands in Fig. 1(b), as described in the text. Their sum (○) represents the total DOS of the d-character in icosahedral $Al_{65}Cu_{20}Os_{15}$.

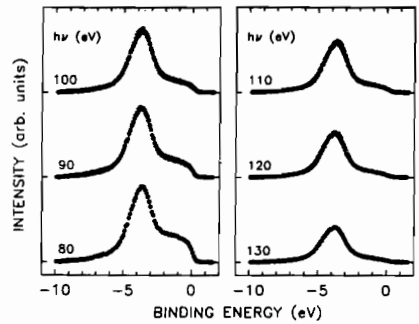

Fig. 3. Comparison of the valence bands generated by using empirical partial Os 5d and Cu 3d DOS from Fig. 2 and the corresponding σ values[7] (●) with the experimental valence bands from Fig. 1(b) (○), as descibed in the text.

opening of a pseudogap at E_F. Such an interpretation, however, is open to criticism because a simple Fermi cut-off, which would be especially important for IA with d-electron elements, also leads to an intensity decrease. From the spectra in Figs. 2 and 4 one can only conclude that they are indicative of a possible opening of a pseudogap at E_F, but they do not prove its existence.

The separation of the above two effects, and thus an unambiguous experimental verification of the possible existence of the predicted pseudogap, is possible only when high-resolution PES and/or SXE experiments, preferably

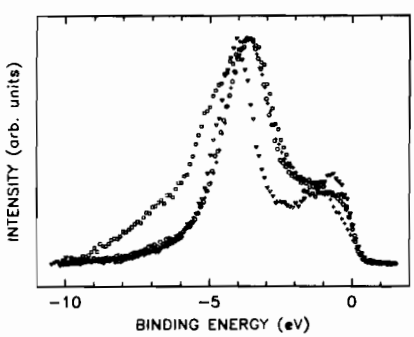

Fig. 4. Valence bands of icosahedral $Al_{65}Cu_{20}Os_{15}$ (○), $Al_{65}Cu_{20}Ru_{15}$ (+), $Al_{65}Cu_{20}Fe_{15}$ (▽), and $Al_{70}Pd_{20}Mn_{10}$ (□) measured respectively at hν=80, 90, 100, and 100 eV.

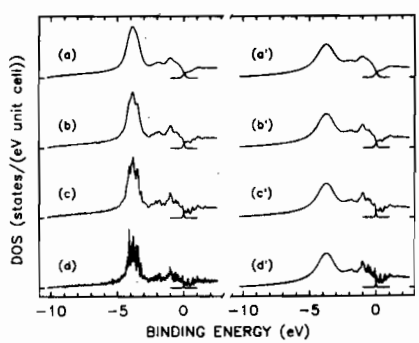

Fig. 5. DOS of an approximant to the icosahedral phase Al-Cu-Fe (Ref. 3) convoluted with (left panel) a Gaussian of different FWHM and (right panel) with a Lorentzian and a Gaussian, as described in the text.

combined with the corresponding inverse PES and/or soft x-ray absorption measurements, are conducted. The energy resolutions of the spectroscopic measurements performed so far were not high enough to warrant the repeated claims[8] of a definite spectroscopic verification of the existence of a pseudogap at E_F. To illustrate this, the theoretical DOS (kindly provided to us by T. Fujiwara) of an approximant[3] to an icosahedral phase Al-Cu-Fe has been first convoluted with a Gaussian of the FWHM equal to 0.4, 0.2, 0.1, and 0.025 eV [(a)-(d) in the left panel of Fig. 5] to account for the instrumental broadening, and then was additionally convoluted with a Lorentzian of the FWHM equal to $\Gamma_L^0(|BE|-E_F)^2$, where Γ_L^0=0.05 eV^{-1}, to account also for the lifetime effects (right panel in Fig. 5). It is clear from Fig. 5 that an energy resolution better than 0.1 eV will be necessary to derive any meaningful information regarding the predicted[3] pseudogap at E_F and the spikiness of DOS.

Acknowledgements

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