SYNCHROTRON-RADIATION STUDIES OF VALENCE BANDS IN STABLE, DECAGONAL Al$_{65}$Co$_{15}$Cu$_{20}$ AND Al$_{70}$Co$_{15}$Ni$_{15}$

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ABSTRACT

Measurements with photoemission spectroscopy in the photon energy range 40-100 eV have been used to make the first determinations of the valence bands of stable, decagonal alloys Al$_{65}$Co$_{15}$Cu$_{20}$ and Al$_{70}$Co$_{15}$Ni$_{15}$. The features due to the transition-metal 3d electronic states have been identified. It has been convincingly demonstrated that, contrary to the prediction of recent band-structure calculations, there is no pseudogap in the density of states at the Fermi level.

1. Introduction

The electrical resistivity in decagonal alloys Al-Co-Cu and Al-Co-Ni is metallic along the periodic direction and exhibits a nonmetallic behaviour, similar to that found in icosahedral alloys, in the quasiperiodic plane.[1-3] Anisotropies in the Hall effect, thermopower, thermal conductivity, and optical conductivity have also been observed.[1,4] Electronic transport properties have been interpreted either in terms of the Hume-Rothery mechanism[1,2] or by invoking a phonon-assisted mechanism.[3] However, recent optical conductivity studies[4] found no evidence for a well developed pseudogap near the Fermi level (E$_F$). On the other hand, the recent band-structure calculations[5] suggest the existence of a well pronounced pseudogap at E$_F$ in the decagonal Al-Co-Cu alloy. In this paper we report the results of the first photoemission spectroscopy (PES) studies of the decagonal alloys Al$_{65}$Co$_{15}$Cu$_{20}$ and Al$_{70}$Co$_{15}$Ni$_{15}$ which clearly demonstrate the absence of a pseudogap at E$_F$.

2. Experimental

Ingots of nominal composition Al$_{65}$Co$_{15}$Cu$_{20}$ and Al$_{70}$Co$_{15}$Ni$_{15}$ were prepared by melting high-purity source metals in an argon atmosphere using an

arc furnace. The ingots were annealed in vacuum at 1073 K for 48 h. The x-ray diffraction study showed that the samples are single phase and exhibit resolution-limited Bragg-peak widths.

Photoemission spectra were collected on beamline U14A at the National Synchrotron Light Source at the Brookhaven National Laboratory. The overall resolution was about 0.6 eV. Other experimental details were the same as described elsewhere.[6] 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.[6] The spectra corrected in such a way can be compared not only with respect to their shape but also in terms of their intensities. This is especially important when the intensity scale of the PES spectra is used, as is the case in this paper, to obtain information on various features in the valence bands and on the partial density of states (DOS) due to a specific element in an alloy.

3. Results and Discussion

The two broad peaks in the valence band of $Al_{65}Co_{15}Cu_{20}$ (Fig. 1) must be predominantly due to the Co and Cu 3d-derived states because the Al sp spectral contribution is much smaller due to the small photoionization cross section, σ, for Al sp orbitals for the photon energies, $h\nu$, used here.[7] To determine the feature due to the Co 3d-like states, a resonant photoemission[6] which involves the Co $3p\rightarrow3d$ transition which occurs at about 59 eV, has been used. It can be seen in Fig. 1 that, as $h\nu$ increases, the relative intensity of the peak at the binding energy (BE) of about -0.7 eV with respect to the peak at about BE=-3.7 eV decreases first, reaches its minimum at $h\nu$ =60 eV, and then starts to increase for higher values of $h\nu$. Since in the vicinity of the Co $3p\rightarrow3d$ transition the changes of σ with $h\nu$ are very small, the suppression of the BE=-0.7 eV feature at $h\nu$ =60 eV indicates that it is mainly of the Co 3d character. This has been additionally confirmed[8] by performing the resonant photoemission in the so-called constant-initial-state mode.[6] It is thus concluded that the features in the valence band of decagonal $Al_{65}Co_{15}Cu_{20}$ located at BE=-0.7(1) eV and BE=-3.7(1) eV are due respectively to the Co 3d and Cu 3d states.

Before the advent of synchrotron radiation as a tunable excitation source, the partial spectral weights due to d or f states of a given element in an alloy, which are generally proportional to the partial DOS associated with a given state of that element, were determined almost exclusively using the soft x-ray emission technique. The use of synchrotron-radiation-based PES allows one also to determine the partial DOS for some orbitals.[8] By taking the difference between the on- ($h\nu$ =63 eV) and off-resonance ($h\nu$ =60 eV) valence bands in Fig. 1, which have been scaled either to the height of the Cu 3d peak or to the height of the Co 3d peak, one obtains respectively the partial DOS of the Co 3d and Cu 3d

character (open circles in Fig. 2), which have been normalized to the corresponding number of 3d electrons per atom. Because of a large scattering in the difference spectra, they were smoothed (closed circles in Fig. 2) to allow for a better comparison with the Co and Cu 3d DOS obtained from theory.[5]
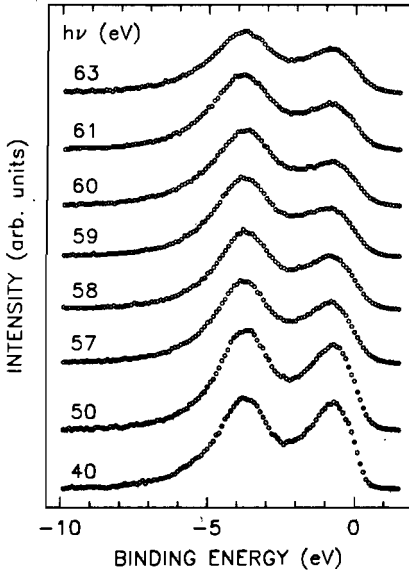

Fig. 1. Valence bands of decagonal $Al_{65}Co_{15}Cu_{20}$ measured for different photon energies hν around the Co 3p–3d transition.

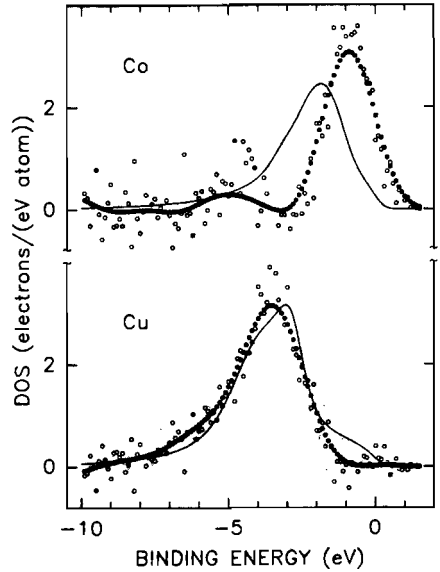Fig. 2. Partial DOS of the Co and Cu 3d states in decagonal $Al_{65}Co_{15}Cu_{20}$ (o) obtained from the hν = 60 eV and 63 eV valence bands in Fig. 1, and later smoothed (●). The broadened theoretical DOS (solid line) is from Ref. 5.

In a recent study the electronic structure of the hypothetical approximant $Al_{60}Co_{14}Cu_{30}$ of a decagonal alloy Al-Co-Cu has been calculated.[5] The theoretical DOS, which was kindly provided to us by T. Fujiwara, exhibits a well pronounced pseudogap at E_F. In order to make a meaningful comparison between a theoretical partial DOS and the partial DOS determined experimentally, the former has to be appropriately broadened to account for the lifetime broadening effects inherent to the PES technique and for the finite resolution of a PES experiment.[6] The theoretical Co 3d and Cu 3d DOS have been convoluted first with a Lorentzian, to account for the lifetime broadening, and then with a Gaussian, to account for the instrumental broadening. The Lorentzian full width at half maximum (FWHM) was taken in the form $\Gamma_L^0(|BE|-E_F)^2$. The Γ_L^0 parameter, which fixes the scale of the broadening, was chosen to be equal to 0.05 eV^{-1} since for

this value one obtains good agreement between the theoretical and experimental widths of the Cu 3d DOS. The Gaussian FWHM was 0.6 eV. As can be seen from Fig. 2, there is a striking disagreement between the theoretical and experimental Co 3d DOS. Contrary to the theoretical prediction of a pronounced Hume-Rothery pseudogap at E_F in the Co 3d DOS, no such pseudogap can be seen in the experimental Co 3d DOS (Fig. 2). In fact, there is a significant Co 3d DOS at E_F, which can be also clearly seen in the valence bands (Fig. 2).

In order to compare the theoretical total DOS with the PES valence band measured at $h\nu = 100$ eV, the theoretical partial Al, Co, and Cu DOS associated with different angular momenta[5] were multiplied by the corresponding σ values[7] and their sum, which represents the theoretical total PES DOS, was broadened in the same way as described above. As can be seen in Fig. 3, there is a significant discrepancy between theory and experiment. In particular, the theory[5]
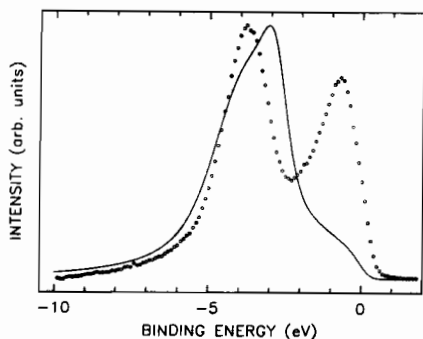

Fig. 3. Comparison between the valence band of decagonal $Al_{65}Co_{15}Cu_{20}$ measured at $h\nu = 100$ eV (o) and the broadened theoretical total DOS (solid line), as described in the text.

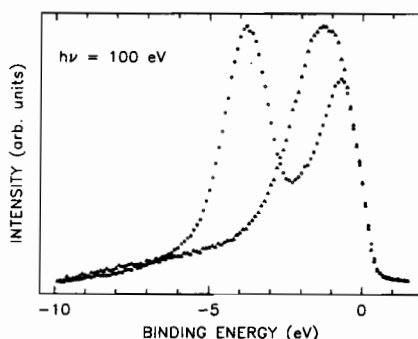Fig. 4. Comparison of valence bands of decagonal $Al_{65}Co_{15}Cu_{20}$ (o) and $Al_{70}Co_{15}Ni_{15}$ ($\triangle$) measured at $h\nu = 100$ eV.

predicts a wide pseudogap around E_F which is clearly not present in the experimental valence band (Fig. 3).

The main feature in the valence band of decagonal $Al_{70}Co_{15}Ni_{15}$ (Fig. 4) results from a strong overlap of the Co 3d and Ni 3d states.[6] A comparison of the valence bands of decagonal $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$ (Fig. 4) shows that there is also no pseudogap at E_F in decagonal $Al_{70}Co_{15}Ni_{15}$; this is similar to the situation in decagonal $Al_{65}Co_{15}Cu_{20}$. It is thus concluded that the PES data clearly show the lack of a pseudogap at E_F in two decagonal alloys of high structural quality, which can be interpreted as evidence that the Hume-Rothery mechanism does not play an important role in the stability and transport properties of decagonal alloys. This agrees with the results of the optical conductivity studies[4] and is at variance with the interpretation of the electronic transport data[1,2] and the prediction based on the energy-band calculations.[5]

Energy-band calculations also predict that a property specific only to quasicrystals is the spikiness of their DOS. This spikiness is expected to be very prominent in icosahedral alloys, and less marked, but still present, in decagonal alloys.[5] The width of a spiky peak is expected to be of the order 0.01-0.02 eV. No such spikiness could be detected in the present investigation. As is discussed in detail elsewhere,[8] such spikiness, if it indeed exists, can be detected only by the PES and inverse PES techniques using superior energy resolutions.

Acknowledgements

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