



ELSEVIER

27 February 1995

PHYSICS LETTERS A

Physics Letters A 198 (1995) 237–242

Are decagonal quasicrystals the Hume–Rothery phases?

Z.M. Stadnik^{a,*}, G.W. Zhang^a, A.-P. Tsai^b, A. Inoue^b^a Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5^b Institute for Materials Research, Tohoku University, Sendai 980, Japan

Received 5 January 1995; accepted for publication 9 January 1995

Communicated by L.J. Sham

Abstract

Photoemission spectroscopy measurements in the photon energy range 40–100 eV have been used to make the first determinations of the valence bands of the high quality decagonal alloys $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$. Within the energy resolution our results reveal that, contrary to the prediction of recent band-structure calculations and to the widespread qualitative interpretation of various electronic transport data, there is no pseudogap in the density of states at the Fermi level. This suggests that decagonal alloys differ significantly in their electronic structure from icosahedral alloys and that a Hume–Rothery mechanism does not play an important role in accounting for their stability and electronic transport properties.

1. Introduction

Quasicrystals are a new form of matter which differ 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 [1]. A central problem in condensed-matter physics is to determine whether quasiperiodicity leads to new physical properties which are significantly different from those of crystalline and amorphous materials. Such unusual properties have been found in icosahedral alloys [2]. Their most striking feature, which is not expected for alloys consisting of normal metallic elements, is the very high value of the electrical resistivity (up to $2 \Omega \text{ cm}$ in the Al–Pd–Re system [3]). This and other unusual electronic transport properties of icosahedral alloys [1,2] have been interpreted *qualitatively* almost exclusively in terms of a Hume–Rothery mech-

anism, which implies the existence of a pseudogap in the vicinity of the Fermi level, E_F ; this is in spite of some doubts about the theoretical justification of this mechanism for quasicrystals [4]. Such an interpretation seems to be supported by the electronic structure calculations performed for the crystalline approximants of icosahedral alloys [5,6]; these calculations predict a structure-induced pseudogap, or rather several pseudogaps, in the density of states, DOS, around E_F . Spectroscopic data based on soft X-ray emission and absorption spectroscopies have been interpreted [7] as direct evidence for the existence of such a pseudogap, in spite of the limitations of the energy resolution used in comparison with the widths of the gaps and the severe lifetime broadening effects inherent to these techniques. It is unclear at present which mechanisms are responsible for the unusual transport properties of icosahedral alloys and to what extent these properties can be associated with the quasiperiodicity.

Quasicrystals of decagonal symmetry combine

* Corresponding author.

two structural characteristics: the atoms are ordered quasiperiodically in planes which are stacked with translational periodicity. As expected, the electrical resistivity in decagonal alloys Al–Co–Cu and Al–Co–Ni has metallic characteristics along the periodic direction, and exhibits a nonmetallic behavior, similar to that observed in icosahedral alloys, in the quasiperiodic plane [8–10].

Anisotropies in the Hall effect, thermopower, thermal conductivity, and optical conductivity have also been observed [8,11]. As is the situation for icosahedral alloys, the transport properties of decagonal alloys have been interpreted qualitatively mainly by invoking the Hume–Rothery mechanism [8,9]. However, some recent optical conductivity data [11] could not be reconciled with the existence of a pseudogap near E_F . This seems to be supported by the conclusion of a recent theoretical free-electron plane-wave model study [12] which showed that the periodicity in the tenfold direction removes or substantially suppresses the gap at E_F in decagonal alloys. On the other hand, recent band-structure calculations [13] of an approximant of a decagonal alloy Al–Co–Cu predict the existence of a well pronounced and very wide pseudogap at E_F . The width of this pseudogap in the occupied DOS is about 1 eV, and should therefore be detected by photoemission spectroscopy (PES) experiments of medium energy resolution (around 0.4 eV). It should be noted that this is in contrast to the situation for icosahedral alloys where the center of the pseudogap is predicted to be located above E_F [5,6], and thus the detection of its narrow width (< 0.1 eV) below E_F is possible only by using high energy-resolution spectroscopic techniques; such high energy-resolution experiments have not been carried out yet.

In this Letter we report the first investigation of the valence bands of two decagonal alloys $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$. We show that there is no pseudogap in the DOS below E_F in the studied alloys within the experimental resolution. The consequences of our experimental results are discussed.

2. Experimental procedure

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

furnace. The ingots were annealed in vacuum as described elsewhere [14]. The X-ray diffraction and electron microscopy studies showed that the samples are single phase and exhibit resolution-limited Bragg-peak widths.

Photoemission spectra were collected on the beamline U14A at the National Synchrotron Light Source at the Brookhaven National Laboratory. The overall resolution was about 0.4 eV. The samples were cleaned in the experimental vacuum chamber by gentle mechanical abrasion using an alumina scraper. The surface cleanliness of the samples was frequently verified by monitoring the appearance of the oxide features in the PES spectra of the Al 2p core-level lines and/or of the valence bands [15]. The base pressure in the experimental chamber was in the high 10^{-11} Torr range. All the spectra presented here were obtained from at least two different regions of the samples studied, and were indistinguishable within the resolution of the experiment. The PES spectra were corrected for the energy dependence of the electron transmission of the electron-energy analyzer, the photon flux, and the secondary-electron background [16]. These corrected spectra can be compared not only with respect to their shape but also in terms of their intensities.

3. Results and discussion

The two broad features in the valence band of $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ (Fig. 1) must be predominantly due to the Co and Cu 3d-derived states because the relatively small photoionization cross section, σ , for Al sp orbitals for the photon energies, $h\nu$, used here reduces the Al sp contribution [17]. The feature associated with the Co 3d-like states can be determined by using a resonant PES which involves the Co 3p \rightarrow 3d transition at $h\nu \approx 59$ eV. 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 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 \rightarrow 3d transition the changes of σ with $h\nu$ are very small [17], the suppression of the BE = -0.7 eV feature at $h\nu = 60$ eV indicates that it is mainly of Co 3d character. This has been confirmed by performing the resonant PES in the so-called constant-initial-state

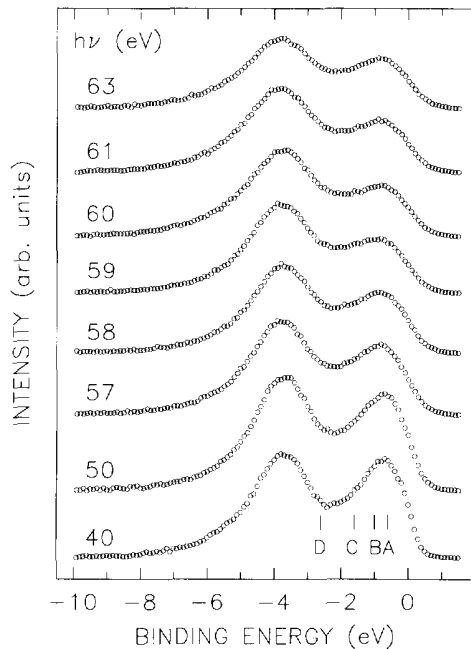


Fig. 1. Valence bands of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ measured for different photon energies $h\nu$ around the Co $3p \rightarrow 3d$ transition. A, B, C, and D identify binding energies for which constant-initial-state spectra were measured (Fig. 2).

mode [16]. As can be seen in Fig. 2, the strongest resonance occurs at $\text{BE} \approx -0.7$ eV. We conclude that the peaks at $\text{BE} = -0.7(2)$ and $-3.7(1)$ eV are respectively due to the Co 3d and Cu 3d states.

It is now widely accepted that PES valence bands measured typically for $h\nu \geq 40$ eV represent the initial DOS weighted by frequency-dependent dipole matrix elements and by the $\sigma(h\nu)$ values for various s, p, d, and f states [18]. To a good approximation, it can be assumed that the matrix elements do not change significantly over the width of the valence bands. Thus the measured PES valence bands, when corrected for experimental factors and for inelastically scattered electrons, are generally proportional to the DOS modulated by the σ values. Before the availability 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

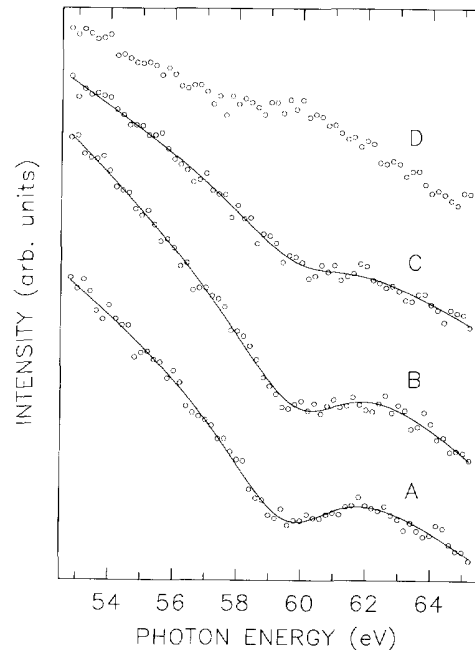


Fig. 2. Constant-initial-state spectra measured for the valence band positions A, B, C, and D in Fig. 1, which are identified here by the same letters. The solid line is a fit to a Fano profile and a linear background [16].

determine the partial DOS for some orbitals [19]. 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. 3); these partial DOSs have been normalized to the corresponding number of 3d electrons per atom. As the difference spectra had a large scatter, they were smoothed (full circles in Fig. 3) to allow a better comparison with the theoretical Co and Cu 3d DOS [13].

In a recent study the electronic structure of the hypothetical approximant $\text{Al}_{60}\text{Co}_{14}\text{Cu}_{30}$ of a decagonal alloy Al–Co–Cu has been calculated [13]. The theoretical DOS, which was kindly provided to us by T. Fujiwara, exhibits a well pronounced pseudogap at E_F [13]. In order to make a meaningful comparison between the theoretical and experimental partial DOS, 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

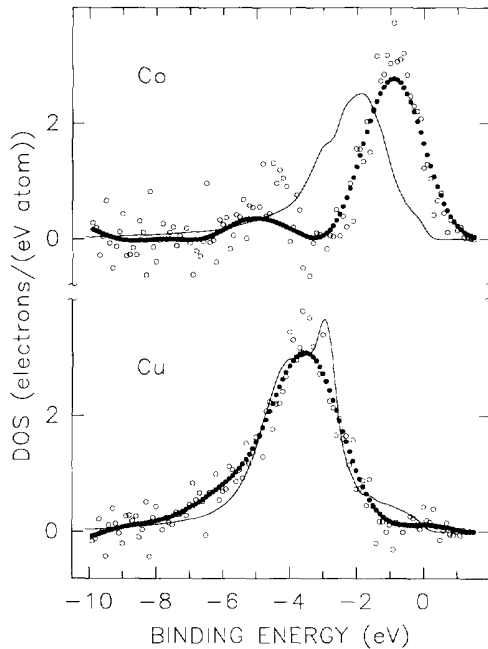


Fig. 3. Partial DOS of the Co and Cu 3d states in decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ (o) obtained from the $h\nu = 60$ eV and 63 eV valence bands in Fig. 1, and later smoothed (•). The broadened theoretical DOS (solid line) is from Ref. [13], as described in the text.

PES experiment. The theoretical Co 3d and Cu 3d DOS were multiplied by the Fermi–Dirac distribution function at room temperature and then convoluted with a Lorentzian, to account for the lifetime broadening, and with a Gaussian, to account for the instrumental broadening. The Lorentzian full width at half maximum (FWHM) was taken in the form $I_L^0(|\text{BE}| - E_F)^2$ [20]. The I_L^0 parameter, which fixes the scale of the broadening, was chosen to be 0.02 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 0.4 eV. As can be seen from Fig. 3, there is a striking disagreement between the theoretical and experimental Co 3d DOS. In contrast 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. 3). In fact, there is a significant Co 3d DOS at E_F , which can be also clearly seen in the valence bands (Fig. 1).

In order to compare the theoretical PES valence

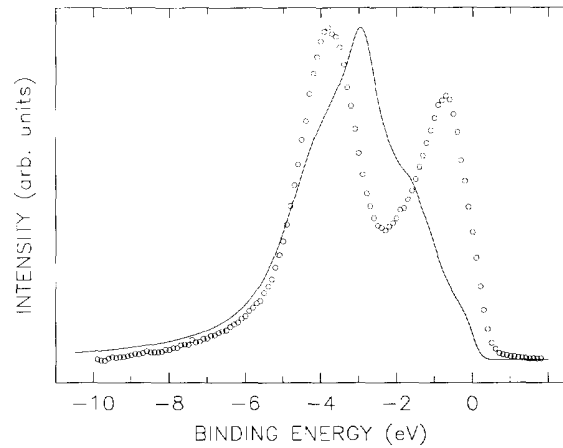


Fig. 4. Comparison between the valence band of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ measured at $h\nu = 100$ eV (o) and the broadened theoretical DOS (solid line) from Ref. [13], as described in the text.

band resulting from the 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 [13] were multiplied by the corresponding σ values [17] and the composition, and then were divided by the corresponding number of electrons [21]. Their sum, which represents the theoretical PES valence band, was broadened in the same way as described above. As can be seen in Fig. 4, there is a significant discrepancy between theory and experiment. In particular, the theory [13] predicts a wide pseudogap around E_F which is clearly not present in the experimental valence band (Fig. 4).

The main feature in the valence band of decagonal $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ (Fig. 5) results from a strong overlap of the Co 3d and Ni 3d states. Because of this overlap, it was not possible to separate the partial DOS associated with the Co and Ni 3d states. A comparison of the valence bands of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ (Fig. 5) shows that there is also no pseudogap at E_F in decagonal $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$, as in the case of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$. We conclude that the PES data are conclusive evidence for the lack of a pseudogap at E_F in two decagonal alloys of high structural quality. This 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 conclusions

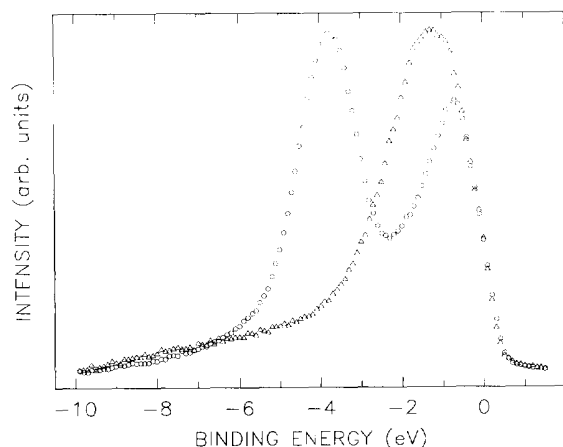


Fig. 5. Comparison of valence bands of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ (\circ) and $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ (\triangle) measured at $h\nu = 100$ eV.

based on the recent results of the optical conductivity [11] and of the theoretical plane-wave model studies [12], and is at variance with the qualitative interpretation of the electronic transport data [8,9] and the prediction based on the energy-band calculations [13].

The lack of a pseudogap at E_F in decagonal alloys means that there is a fundamental difference between their electronic structure and that of icosahedral alloys, in which this pseudogap seems to exist [1,2,5–7]. Therefore, one has to consider other unconventional mechanisms to account for the unusual physical properties of decagonal alloys. Perhaps a more quantitative approach based on the ideas of the so-called compartmentalization [4] or of the intraband transitions via electron hopping descriptions [22] could lead to a better understanding of the electronic structure of decagonal alloys. The criticality of wave functions [23] or a description of quasicrystals as a hierarchy of clusters [24] may also play an important role.

4. Conclusions

The structure of the valence band of decagonal $\text{Al}_{65}\text{Co}_{15}\text{Cu}_{20}$ consists of two main features with the maximum intensity at 0.7(2) and 3.7(1) eV below E_F . The first feature was shown to be due to the Co 3d-derived states, whereas the second feature originates from the Cu 3d-like states. The location of the feature associated with the Co 3d-derived states is the

same in the valence band of decagonal $\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$ and these states strongly overlap with the states of Ni 3d character. We show that within the experimental resolution, contrary to the prediction of recent band-structure calculations and the widespread qualitative interpretation of electronic transport data of decagonal alloys, there is no pseudogap at E_F in the studied alloys. A Hume–Rothery mechanism cannot therefore be invoked to account for the stability and transport properties of decagonal alloys. Other unconventional mechanisms, which are mentioned, may be responsible for the unusual properties of these alloys.

Acknowledgement

This work was supported by the Natural Sciences and Engineering Research Council of Canada and by the Ministry of Education, Science, and Culture of Japan. The research was carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (DOE contract No. DE-AC02-76-CH00016). Two of us (Z.M.S. and G.W.Z.) are indebted to Dr. M.-L. Shek for her help in performing the PES experiments.

References

- [1] C. Janot, *Quasicrystals: A primer* (Oxford Univ. Press, Oxford, 1992); in: *Quasicrystals, the state of the art*, eds. D.P. DiVincenzo and P.J. Steinhardt (World Scientific, Singapore, 1991); in: *Quasicrystals*, eds. T. Fujiwara and T. Ogawa (Springer, Berlin, 1990).
- [2] S. Takeuchi, *Mater. Sci. Forum* 150/151 (1994) 35, and references therein; S.J. Poon, *Adv. Phys.* 41 (1992) 303.
- [3] Y. Honda, K. Edagawa, A. Yoshika, T. Hashimoto and S. Takeuchi, *Japan. J. Appl. Phys. A* 33 (1994) 4929, and references therein.
- [4] J.C. Phillips, *Phys. Rev. B* 47 (1993) 7747.
- [5] G. Trambly de Laissardière and T. Fujiwara, *Phys. Rev. B* 50 (1994) 5999, and references therein.
- [6] M. Windisch, M. Krajčí and J. Hafner, *J. Phys. Condens. Matter* 6 (1994) 6977, and references therein.
- [7] E. Belin, Z. Dankhazi and A. Sadoc, *Mater. Sci. Eng. A* 181/182 (1994) 717, and references therein.
- [8] W. Yun-ping and Z. Dian-lin, *Phys. Rev. B* 49 (1994) 13204, and references therein.

- [9] W. Yun-ping, Z. Dian-lin and L.F. Chen, Phys. Rev. B 48 (1993) 10542.
- [10] S. Martin, A.F. Hebard, A.R. Kortan and F.A. Thiel, Phys. Rev. Lett. 67 (1991) 719.
- [11] D.N. Basov, T. Timusk, F. Barakat, J. Greedan and B. Gruschko, Phys. Rev. Lett. 72 (1994) 1937.
- [12] R.F. Sabiryanov and S.K. Bose, J. Phys. Condens. Matter 6 (1994) 6197.
- [13] G. Trambly de Laissardière and T. Fujiwara, Mater. Sci. Eng. A 181/182 (1994) 722; Phys. Rev. B 50 (1994) 9843.
- [14] A.-P. Tsai, A. Inoue and T. Masumoto, Mater. Trans. Japan. Inst. Met. 30 (1989) 300, 463.
- [15] Z.M. Stadnik and G. Stroink, Phys. Rev. B 47 (1993) 100.
- [16] G.W. Zhang, Z.M. Stadnik, A.-P. Tsai and A. Inoue, Phys. Rev. B 50 (1994) 6696.
- [17] J.-J. Yeh, Atomic calculation of photoionization cross-sections and asymmetry parameters (Gordon and Breach, New York, 1993).
- [18] D.E. Eastman and W.D. Grobman, Phys. Rev. Lett. 28 (1972) 1327;
J. Freeouf, M. Erbudak and D.E. Eastman, Solid State Commun. 13 (1973) 771;
P.J. Feibelman and D.E. Eastman, Phys. Rev. B 10 (1974) 4932.
- [19] J.W. Allen, S.J. Oh, O. Gunnarsson, K. Schönhammer, M.B. Maple, M.S. Torikachvili and I. Lindau, Adv. Phys. 35 (1986) 275.
- [20] H. Höchst, P. Steiner, G. Reiter and S. Hüfner, Z. Phys. B 42 (1981) 199.
- [21] A. Goldmann, J. Tejada, N.J. Shevchik and M. Cardona, Phys. Rev. B 10 (1974) 4388;
J. Tejada, N.J. Shevchik, W. Braun, A. Goldmann and M. Cardona, Phys. Rev. B 12 (1975) 1557.
- [22] D. Mayou, C. Berger, F. Cyrot-Lackmann, T. Klein and P. Lanco, Phys. Rev. Lett. 70 (1993) 3915.
- [23] H. Tsunetsugu, T. Fujiwara, K. Ueda and T. Tokihiro, Phys. Rev. B 43 (1991) 8879;
B. Passaro, C. Sire and V.G. Benza, Phys. Rev. B 46 (1992) 13751.
- [24] C. Janot and M. de Boissieu, Phys. Rev. Lett. 72 (1994) 1674.