Synchrotron-radiation study of valence bands in icosahedral $Al_{65}Cu_{20}Fe_{15}$ and crystalline Al_7Cu_2Fe

Zbigniew M. Stadnik [a] and Gerhard Stroink [b]

[a] *Ottawa–Carleton Institute for Physics, Department of Physics, University of Ottawa, Ottawa, ON K1N 6N5, Canada*
[b] *Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada*

Measurements with photoemission spectroscopy have shown that the valence bands of the stable icosahedral $Al_{65}Cu_{20}Fe_{15}$ and its crystalline counterpart Al_7Cu_2Fe are very similar. No unusual features in the valence band of icosahedral $Al_{65}Cu_{20}Fe_{15}$ which could be ascribed to its quasiperiodic nature are observed. The results support a two-block structural model of icosahedral $Al_{65}Cu_{20}Fe_{15}$ and are indicative of the presence of an energy gap in the density of states at the Fermi level.

1. Introduction

The dramatic discovery of an icosahedral Al–Mn alloy by Shechtman et al. [1] extended the dichotomous division of solids into either crystalline or amorphous, by introducing the notion of quasicrystals. This new form of matter has long-range quasiperiodic order and long-range orientational order of crystallographically forbidden symmetries. A central problem in solid-state physics is to determine whether this new quasiperiodic structure leads to expected novel physical properties found neither in crystalline nor in amorphous materials. In particular, there is considerable current interest in determining the electronic structure of quasicrystals since this is crucial to our understanding of other physical properties.

The quasiperiodic nature of these new materials makes calculations of their electronic structure a challenging endeavour. For 1D and 2D quasicrystals, singular features in wave-functions and energy spectra have been predicted [2,3]. For more realistic 3D quasicrystals, theoretical elec-

Correspondence to: Dr Z.M. Stadnik, Department of Physics, University of Ottawa, Ottawa, ON K1N 6N5, Canada. Tel: +1-613 564 8276. Telefax: +1-613 564 6712.

tronic structure calculations based on various approximate schemes (a review of such calculations is given in ref. [4]) lead to contradictory predictions. A high density of states (DOS) at the Fermi level, E_F, and several distinct peaks below E_F have been suggested using icosahedral clusters of Al and Al–Mn to mimic an icosahedral alloy [5]. However, some recent calculations [6] for Al–Cu–(Li, Mg) clusters show that the DOS (E_F) can be substantially decreased by the presence of vacant centres. Pseudopotential calculations [7] have indicated singularities and special features in the DOS of a nearly-free-electron quasicrystal. However, calculations based on modelling an icosahedral (i) alloy with a 3D Penrose lattice have shown [8] no special features in the DOS induced by quasiperiodicity. On the other hand, calculations of the electronic structure of the crystalline (c) approximants of i alloys [9] suggest the existence of a universal pseudo-gap at E_F which satisfies the Hume-Rothery relation. They also indicate that the structure of the DOS is very spiky.

The electronic structure of i alloys has been studied experimentally mainly via specific heat measurements [10]. From the measured electronic specific heat coefficient, γ, the DOS (E_F) can be estimated. The main result of these stud-

ies is the observation of the reduced DOS (E_F) in stable i alloys as compared with the free-electron value, and of the closeness between the DOS (E_F) values in metastable i alloys, their c counterparts and the corresponding free-electron values. This has been interpreted as evidence for similarities between the electronic structures of i alloys and their c counterparts, and as an indication for the existence of a minimum in the DOS at E_F in stable i alloys.

To determine any possible unusual features in the DOS of i alloys, one needs information on the DOS not only at E_F but also below and above that energy. Therefore, studies using spectroscopic techniques which probe the DOS at energies in the vicinity of E_F are very useful. Unfortunately, the first such study using soft X-ray emission (SXE), soft X-ray absorption (SXA), and X-ray photoelectron spectroscopy (XPS) was performed on oxidized i Al–Mn alloys [11]. Subsequent SXE experiments on Al–Mn [12,13], Al–Cu–Li and Al–Cu–Mg i alloys [13,14] found that the spectra of i alloys are similar to those of the corresponding c alloys. This similarity was interpreted as evidence for the absence of exotic features induced by i symmetry. Recent photoemission and inverse photoemission investigations of the stable i-Al–Li–Cu alloy and its corresponding Frank–Kasper c phase [15] found a gap-like feature in the DOS just above E_F, which agrees with the theoretical predictions [9]. Recently the valence band of i-Al$_{65}$Cu$_{21}$Fe$_{14}$ was studied with photoemission for various incident photon energies [16]. It was suggested that a large peak at 4 eV was due to Cu 3d states, but the origin of the feature at about 1 eV was not determined. Some resonances were claimed to have been observed, but no supportive data were presented. The main conclusion was the apparent observation of the gap-like anomaly in the DOS near E_F.

It has often been argued that the presence of intrinsic phason disorder in metastable i alloys obscures subtle features in their electronic structure induced by i symmetry. To avoid this possible influence of phason disorder, the thermodynamically stable Al$_{65}$Cu$_{20}$Fe$_{15}$ i alloy, which is known to be the most perfect quasicrystal [17], was chosen for the present study. In order to

demonstrate any possible exotic features in the electronic structure of i-Al$_{65}$Cu$_{20}$Fe$_{15}$, it is essential to compare these features with those present in the electronic structure of the c alloy closest in composition to the studied i alloy. The only ternary c alloy of nearby composition is Al$_7$Cu$_2$Fe, which was therefore also investigated.

2. Experimental procedure

Alloys of composition Al$_{65}$Cu$_{20}$Fe$_{15}$ and Al$_7$Cu$_2$Fe were produced by arc-melting in argon of high-purity elemental constituents. They were cut into slices suitable for photoemission measurements and were vacuum annealed at 1000 K for 2 days [4]. All the peaks in the X-ray diffraction spectra of Al$_{65}$Cu$_{20}$Fe$_{15}$ and Al$_7$Cu$_2$Fe could be indexed respectively to the icosahedral phase [18] and on the basis of a tetragonal unit cell [19]. The details of the X-ray diffraction analysis have been given elsewhere [4].

Photoemission spectra were collected on beamline U14A at the National Synchroton Light Source at Brookhaven National Laboratory. Photon energies between 40 and 160 eV were selected with a plane grating monochromator and the electrons were analyzed at near-normal emission with a PHI 15-255 precision electron energy analyzer. The resulting overall resolution was 0.4–0.5 eV. The samples were cleaned in the experimental vacuum chamber by frequent vigorous mechanical abrasion using an alumina scraper. Their surface cleanliness was frequently checked by monitoring the Al 2p line [4,20]. Argon ion bombardment was not used for surface cleaning since it could alter the surface stoichiometry of the samples. The base pressure in the experimental chamber was 2×10^{-10} Torr. All the spectra presented in this study were obtained from at least two different regions of the samples studied, and turned out to be indistinguishable within the resolution of the experiment. No smoothing or any other corrections were performed on the spectra and each spectrum has been normalized to give a constant height between the maximum and minimum recorded count.

3. Results and discussion

The structure of the valence-band spectra of i-$Al_{65}Cu_{20}Fe_{15}$ is not very sensitive to the excitation energy (fig. 1). It consists of two broad features: a peak A at about 0.7 eV and a peak B at about 4.0 eV below E_F. The intensity at E_F is low and no unusual features can be seen (fig. 1).

The origin of various features in a valence band of an alloy can in principle be determined by the use of tunable synchrotron radiation [21]. For transition-metal elements, the resonance occurs at excitation energies near the 3p threshold. In order to identify the contribution to the valence band of i-$Al_{65}Cu_{20}Fe_{15}$ due to Fe 3d states, resonant photoemission spectra were measured in the vicinity of the Fe 3p → 3d transition at about 53 eV (fig. 2). The feature A at 0.7 eV exhibits a prominent resonance. With increasing photon energy, its intensity first decreases (fig. 2), reaches its minimum at photon energy of 53 eV, and then increases. We conclude that the feature A at 0.7 eV in the valence band of i-$Al_{65}Cu_{20}Fe_{15}$ (figs. 1 and 2) contains a significant contribution from the Fe 3d states.
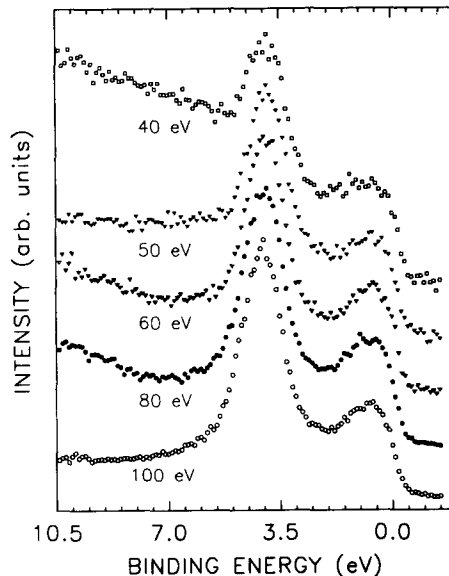

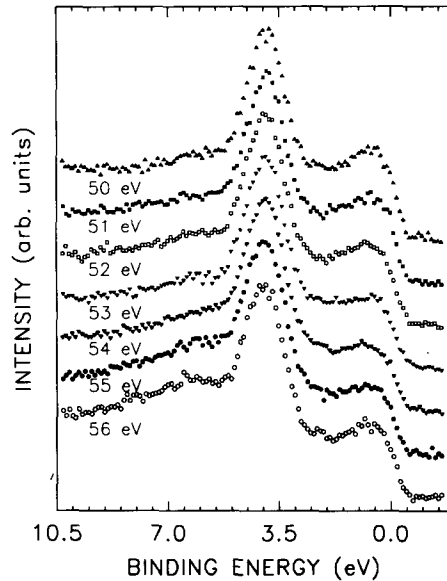
Fig. 2. Valence-band spectra of i-$Al_{65}Cu_{20}Fe_{15}$ for photon energies near the Fe 3p → 3d excitation region.

Although it was not possible to measure the valence-band spectra near the Cu 3p → 3d transition because of the second-order light from the monochromator, the contribution of the Cu 3d states to the valence band can be identified using available data and the arguments given below. A comparison of the valence-band spectrum of i-$Al_{65}Cu_{20}Fe_{15}$ (figs. 1 and 2) with the spectra of Cu metal and Cu–Fe and Al–Cu c alloys (see, for example, fig. 4 in ref. [22] and fig. 1 in ref. [23]) shows that the feature B at 4.0 eV (figs. 1 and 2) is mainly due to the Cu 3d states. Taking into account the shape of the valence band of Al [24] and enormous differences in the photoionization cross-sections for Al 3p, and Cu and Fe 3d electrons [25], it can be concluded that the Al 3p states contribute to a broad plateau-like background onto which the features A and B are superimposed (figs. 1 and 2).

The valence-band spectra of c-Al_7Cu_2Fe measured at the same photon energies as those of i-$Al_{65}Cu_{20}Fe_{15}$ (fig. 1) are shown in fig. 3. It is noticeable from the comparison of figs. 1 and 3 that the structure of the valence bands of the i-$Al_{65}Cu_{20}Fe_{15}$ and c-Al_7Cu_2Fe is essentially the same. This is clearly demonstrated in fig. 4 in

Fig. 1. Valence-band spectra of i-$Al_{65}Cu_{20}Fe_{15}$ for photons of different energies.
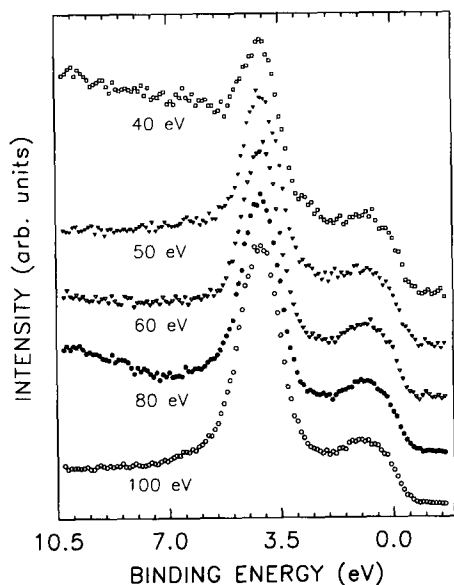
Fig. 3. Valence-band spectra of c-Al$_7$Cu$_2$Fe for photons of different energies.

which the valence-band spectra of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ and c-Al$_7$Cu$_2$Fe measured at photon energy of 100 eV are overlapped. The larger intensity of the feature A in the spectrum of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ as compared with the corresponding intensity in
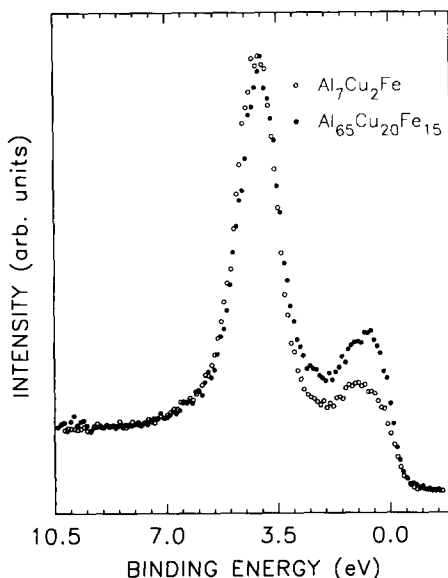

Fig. 4. Valence-band spectra of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ and c-Al$_7$Cu$_2$Fe measured at a photon energy of 100 eV.

the spectrum of c-Al$_7$Cu$_2$Fe (fig. 4) reflects a larger Fe content in the i alloy than in the c alloy. This constitutes additional evidence that the feature A originates primarily from the Fe 3d states. The close similarity of the valence bands of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ and c-Al$_7$Cu$_2$Fe indicates that the electronic structures of these two alloys must be very much alike. This also suggests that the i symmetry does not induce any unusual features of width greater than about 0.4 eV in the valence band of i-Al$_{65}$Cu$_{20}$Fe$_{15}$.

The above conclusion regarding the strong similarity of the electronic structures of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ and c-Al$_7$Cu$_2$Fe can be also interpreted as a supportive argument for a structural model of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ put forward by Phillips and Rabe [26], which explains transport anomalies observed in stable i alloys. This model assumes that the internal structure of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ consists of two blocks. The first block is the icosahedral one and has electronic properties similar to the s–p type, i.e., free-electron-like i alloys, whereas the second block is derived from the c-Al$_7$Cu$_2$Fe. One can thus argue that the contribution of the first block to the valence band of i-Al$_{65}$Cu$_{20}$Fe$_{15}$ alloy would be in the form of a s–p type band, whereas the contribution of the second block would result in the features characteristic for c-Al$_7$Cu$_2$Fe. This is what is indeed observed here (fig. 4).

The low intensity at E_F (fig. 4) indicates that the DOS (E_F) must be relatively small. Although a distinct gap-like structure located close to E_F is not observed within the experimental resolution, the strong decrease of intensity towards E_F is indicative that such a structure may exist. To prove this unambiguously, additional spectra of unoccupied states above E_F would have to be measured with inverse photoemission spectroscopy.

(DOE contract number of DE-AC02-76CH00016).

References

[1] D. Shechtman, I. Blech, D. Gratis and J.W. Cahn, Phys. Rev. Lett. 53 (1984) 1951.

[2] H. Hiramoto and M. Kohmoto, Phys. Rev. Lett. 62 (1989) 2714, and references therein.

[3] T. Tokihiro, Phys. Rev. B40 (1989) 2889, and references therein.

[4] Z.M. Stadnik and G. Stroink, Phys. Rev. B47 (1993) 100.

[5] M.E. McHenry, M.E. Eberhart, R.C. O'Handley and K.H. Johnson, Phys. Rev. Lett. 56 (1986) 81.

[6] Y. Jinlong, W. Kelin, L.F. Donà dalle Rose and F. Toigro, Phys. Rev. B44 (1991) 4275.

[7] A.P. Smith and N.W. Ashcroft, Phys. Rev. Lett. 59 (1987) 1365.

[8] M.A. Marcus, Phys. Rev. B34 (1986) 5981;
M. Krajčí and T. Fujiwara, Phys. Rev. B38 (1988) 12903.

[9] T. Fujiwara, Phys. Rev. B40 (1989) 942; J. Non-Cryst. Solids 117&118 (1990) 844; in: Quasicrystals, ed. T. Fujiwara and T. Ogawa (Springer, Berlin, 1990) p. 196; T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. 66 (1991) 333.

[10] B.D. Biggs, S.J. Poon and N.R. Munirathnam, Phys. Rev. Lett. 65 (1990) 2700;
U. Mizutani, A. Kamiya, T. Matsuda, K. Kishi and S. Takeuchi, J. Phys. Condens. Matter 3 (1991) 3711, and references therein.

[11] A. Traverse, L. Dumoulin and E. Belin, in: Quasicrystalline Materials, ed. Ch. Janot and J.M. Dubois (World Scientific, Singapore, 1988) p. 399.

[12] E. Belin and A. Traverse, J. Phys. Condens. Matter 3 (1991) 2157.

[13] D.L. Ederer, R. Schaefer, K.-L. Tsang, C.H. Zhang, T.A. Callcott and E.T. Arakawa, Phys. Rev. B37 (1988) 8594.

[14] P.A. Bruhwiler, J.L. Wagner, B.D. Biggs, Y. Chen, K.M. Wong, S.E. Schnatterly and S.J. Poon, Phys. Rev. B37 (1988) 6529.

[15] H. Matsubara, S. Ogawa, T. Kinoshita, K. Kishi, S. Takeuchi, K. Kimura and S. Suga, Jpn. J. Appl. Phys. 30 (1991) L389.

[16] M. Mori, S. Matsuo, T. Ishimasa, T. Matsuura, K. Kamiya, H. Inokuchi and T. Matsukawa, J. Phys. Condens. Matter 3 (1991) 767.

[17] Y. Calvayrac, A. Quivy, M. Bessière, S. Lefebvre, M. Cornier-Quiquandon and D. Gratias, J. Phys. (Paris) 51 (1990) 417;
A. Waseda, K. Edagawa and H. Ino, Philos. Mag. Lett. 62 (1990) 183.

[18] P.A. Bancel, P.A. Heiney, P.W. Stephens, A.I. Goldman and P.M. Horn, Phys. Rev. Lett. 54 (1985) 2422.

[19] M.G. Brown and P.J. Brown, Acta Crystallogr. 9 (1956) 911.

[20] S.A. Flodstrom, R.Z. Bachrach, R.S. Bauer and S.B.M. Hagström, Phys. Rev. Lett. 37 (1976) 1282;
N.A. Braaten, J.K. Grepstad and S. Raaen, Surf. Sci. 222 (1989) 499.

[21] L.C. Davis, J. Appl. Phys. 59 (1986) R25, and references therein.

[22] J.C. Fuggle, L.M. Watson, D.J. Fabian and P.R. Norris, Solid State Commun. 13 (1973) 507.

[23] M. Ushida, K. Tanaka, K. Sumiyama and Y. Nakamura, J. Phys. Soc. Jpn. 58 (1989) 1725.

[24] P. Steiner, H. Höchst, W. Steffen and S. Hüfner, Z. Phys. B38 (1980) 191.

[25] J.J. Yeh and I. Lindau, At. Data Nucl. Data Tables 32 (1985) 1.

[26] J.C. Phillips and K.M. Rabe, Phys. Rev. Lett. 66 (1991) 923.