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Electronic structure of icosahedral $Al_{65}Cu_{20}Fe_{15}$ and crystalline Al_7Cu_2Fe studied by photoemission spectroscopy

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The electronic structure properties of stable icosahedral $Al_{65}Cu_{20}Fe_{15}$ and crystalline Al_7Cu_2Fe are studied with synchrotron-radiation-based photoemission spectroscopy for photon energies between 40 and 160 eV. The valence-band spectra of both alloys do not change significantly with photon energy and their structure is essentially identical. The feature at 0.7 eV below the Fermi level is shown, by employing resonant photoemission near the Fe $3p$ threshold, to be due mainly to Fe $3d$ states, and the feature at 4.0 eV originates primarily from Cu $3d$ states. No unusual features in the valence band of the icosahedral $Al_{65}Cu_{20}Fe_{15}$ alloy, which could be associated with its quasicrystalline nature, are observed within the energy resolution of the experiment. A rapid decrease of the intensity towards the Fermi level is interpreted to be indicative of the existence of a minimum in the density of states at the Fermi level. It is argued that the similar electronic structure of the alloys supports a recently proposed structural model of icosahedral $Al_{65}Cu_{20}Fe_{15}$. A review of published experimental data on the electronic structure of quasicrystals and a survey of various theoretical analyses are also presented.

I. INTRODUCTION

Until a few years ago it was believed that solids could only exist in two basic forms: crystalline and amorphous (glassy). The dramatic discovery by Shechtman *et al.*[1] extended this classification by introducing the notion of quasicrystals—a form of matter exhibiting classically forbidden symmetries (icosahedral, octagonal, decagonal, and dodecagonal). A current problem in condensed-matter physics is to determine how this quasiperiodic structure affects various physical properties of a material, and its electronic structure in particular. It is expected that quasiperiodicity should lead to some exotic physical properties found neither in crystalline nor in amorphous alloys.

From a theoretical point of view, the electronic structure characteristics of three-dimensional (3D) quasicrystals are difficult to calculate, since the absence of translational periodicity in these materials precludes the use of conventional k-space electronic structure methods. The situation is additionally complicated by the fact that the problem of the atomic structure of quasicrystals, and in particular the positions of atoms within this structure, is an open question. Various approximate schemes applied to one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) quasicrystals have therefore been used for calculations of their electronic structure. For 1D quasicrystal (the Fibonacci chain), singular features of the energy spectra and of the wave functions have been demonstrated.[2] The main conclusion of these 1D calculations[2] is that the wave functions are critical, i.e., neither extended nor localized; this corresponds to the singular continuous energy spectra. Singular features in the electronic structure characteristics have been also predicted for 2D quasicrystals (the Penrose lattice).[3-7] In particular, the presence of many energy gaps, as reflected in the spikiness of the density of states (DOS), has been predicted.[3,7] Although it is not clear how applicable such 1D and 2D calculations are for real quasicrystals, they seem to indicate the presence of unusual features in the electronic structure of these materials.

The electronic structure of 3D quasicrystals has been modeled in several ways. In one approach based on mimicking the real icosahedral (i) alloys by Al and Al-Mn clusters of i symmetry, high DOS at the Fermi level (E_F) and several distinct peaks in the DOS, have been predicted.[8] However, similar calculations performed for Co i clusters showed no peculiarities in the DOS that could be directly related to i symmetry. Recent electronic structure calculations of i Al-Cu-(Li,Mg) clusters[10] have shown that the DOS at E_F can be decreased by the presence of vacant centers in the clusters. Electronic structure calculations assuming that quasicrystals can be modeled by 3D Penrose lattices,[7,11] showed no particular features in the DOS due to quasiperiodicity. Marcus concluded[7] that the DOS of the 3D Penrose lattice is not very different from that of a crystal lattice. In another approach, a pseudopotential method was used to calculate the DOS of a quasicrystal with nearly free electrons.[12] Singularities and special features in the DOS were predicted and attributed to i symmetry. It was also argued[12,13] that the stability of such a quasicrystal can be explained by band-structure effects, i.e., that the quasicrystal obeys the Hume-Rothery relations. The fourth approach used to predict the electronic structure of quasicrystals is based on the electronic structure calculations of their crystalline (*c*) analogues (approximants). This method has been applied to Al-Mn (Refs. 14 and 15), Al-Cu-Li (Refs. 15 and 16), and Al-Fe (Refs. 15 and 16) systems. These calculations[14–16] demonstrate that, contrary to the predictions based on clusters calculations,[8] there is a universal, i.e., independent of composition, pseudogap at E_F in quasicrystals. This pseudogap satisfies the Hume-Rothery relation: small changes in an alloy composition lead to a shift of E_F to the exact minimum of the pseudogap, which causes an enhancement of cohesive energies. The DOS consists of many, very narrow, spikes. Our brief review shows that theoretical calculations lead to contradictory predictions (for example, high versus low DOS at E_F, or spiky structure of DOS versus featureless DOS). There is clearly a need for experimental data on the electronic structure, especially on the DOS below and above E_F.

On the experimental side, most published electronic structure data are based on specific heat measurements. These measurements provide the value of the electronic specific heat coefficient γ from which the DOS at E_F, DOS (E_F), can be estimated. Certain general trends can be noticed. The values of DOS (E_F) in *metastable i* systems of Al-Cu-Mg (Refs. 17-21), Al-Zn-Mg (Refs. 21-23), and Al-Ag-Mg (Refs. 20 and 21) are similar to those of corresponding Frank-Kasper *c* systems and are close to the free-electron values. Also in the metastable *i* Al-Cu-V system the DOS (E_F) is close to the free-electron value.[24] On the other hand, a substantial reduction of the DOS (E_F), as compared with the free-electron value, was observed in both *stable i* and corresponding Frank-Kasper systems of Al-Cu-Li (Refs. 17, 18, 21, and 25) and Ga-Zn-Mg (Refs. 19–21 and 24). Significant reduction of DOS (E_F) was also found in stable *i* systems of Al-Cu-Fe (Refs. 24 and 26) and Al-Cu-Ru (Refs. 27 and 28).

The closeness of the DOS (E_F) values in the *i* systems mentioned above and their Frank-Kasper counterparts was interpreted as evidence of the similarity between these systems and the corresponding Frank-Kasper phases.[21] It was also suggested[24,27] that the small values of γ found in stable Al-Cu-Li, Ga-Zn-Mg, Al-Cu-Fe, and Al-Cu-Ru *i* alloys implies that the Fermi level lies very close to, or is at a minimum in the DOS, which would help to stabilize the *i* structure. This conclusion is in agreement with the theoretically predicted[14–16] existence of a pseudogap in the DOS at E_F and at variance with another theoretical prediction[3,8] of the high value of DOS (E_F) in *i* alloys.

While there is general agreement on the values of γ in the above-mentioned *i* systems, some controversial results were published on these values in Al-Mn and Al-Mn-Si *i* alloys. Some results are interpreted in terms of high values of DOS (E_F),[29] whereas the others claim the opposite.[30,31] It seems that the controversy can be resolved if one takes into account an additional contribution[31] to the measured γ due to the occurrence of the spin-glass state in these *i* systems. When this is taken into account, the value of DOS (E_F) turns out to be lower than in the *c* AlMn solid solution, i.e., no high DOS (E_F) is observed,[31] which is at variance with the prediction based on clusters calculations.[8]

Although specific heat measurements are very useful for elucidating electronic properties of an alloy, it should be remembered that they provide information only on the DOS at one particular energy E_F. One needs, however, more complete information on the DOS, both below and above E_F, to determine whether quasiperiodicity indeed induces unusual features in the electronic structure of *i* alloys. Therefore, the use of spectroscopic techniques that probe energy levels below and above E_F is highly desirable. There are only a few reports using such techniques on the electronic structure of quasicrystals. In the first preliminary study of Al-Mn *i* alloys with soft x-ray emission (SXE) and soft x-ray absorption (SXA) spectroscopies, Al *p* states below and above E_F were investigated.[32] Unfortunately, the samples used were substantially oxidized, so the conclusion reached should be treated with some caution. The main result of this work[32] seems to be the observation of the small differences between the SXE and SXA spectra of *i* Al-Mn and their *c* and amorphous counterparts and the conclusion that the DOS (E_F) in the Al-Mn *i* alloys is lower than that in the Al metal. The latter observation, which is in agreement with the specific heat experimental results discussed above and at variance with the theoretical prediction,[8] was subsequently confirmed by two other SXE studies of Al-Mn *i* alloys.[33,34] The SXE investigations of Al-Mn (Refs. 34) and Al-Cu-Li, and Al-Cu-Mg *i* alloys[17] also demonstrated the close similarity between the spectra of *i* alloys and the corresponding *c* systems. This was interpreted as evidence of the lack of unusual features induced by quasiperiodicity. These studies also showed very small shifts of E_F in *i* alloys in comparison to that in corresponding *c* systems,[33,34] which is again contrary to the theoretical result of McHenry *et al.*,[8] who predicted the large (0.8 eV), and experimentally easy detectable, shift to lower energy as the symmetry changes from octahedral to icosahedral.

A previous x-ray photoelectron spectroscopy experiment[32] reported on Al-Mn *i* alloys was performed on oxidized samples. Only core-level lines were measured and no spectra were presented.[32] The authors[32] found no energy shift of the Al 2*s* and 2*p* lines in *i* Al-Mn in comparison with the lines in pure Al, and reported the shift of -1.6 eV of the Mn 3*p* lines relative to the line in pure Mn. No definite conclusions were presented.[32] In a recent letter Mori *et al.*[35] reported on studies of the valence band of *i* $Al_{65}Cu_{21}Fe_{14}$ for various incident photon energy. The main feature in the band at 4 eV below E_F was suggested[35] to originate from 3*d* Cu electrons. The origin of another 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 of that study is the apparent observation of the diplike anomaly in the DOS near E_F, which is in accordance with the specific heat results[24,26] and some theoretical predictions[14–16] discussed above.

Most of the *i* alloys studied so far were *metastable* systems, which possess a significant amount of intrinsic disorder. It was argued that this disorder might smooth any possible unusual features in the DOS introduced by quasiperiodicity and inhibit their experimental observation. Some experimental data seem to support such an argument. For example, the conductivities of metastable i alloys are typically in the range 5000–20 000 $\Omega^{-1}\,\mathrm{cm}^{-1}$ (Refs. 25 and 27), whereas those of stable i alloys can be of the order of 100 $\Omega^{-1}\,\mathrm{cm}^{-1}$ (Refs. 26 and 27). In other words, as the quality of the i samples improves (the amount of disorder decreases), the conductivity dramatically decreases, which is in contrast to the usual behavior in c metallic alloys. For this reason we chose for the present study the stable $Al_{65}Cu_{20}Fe_{15}$ i alloy. In order to establish any possible unusual features in the electronic structure of i $Al_{65}Cu_{20}Fe_{15}$ it is necessary to compare them to the features in the electronic structure of a c alloy(s) of a similar composition(s). The only c alloy of nearby composition is Al_7Cu_2Fe, which we therefore also chose to investigate.

II. EXPERIMENT

Ingots of compositions $Al_{65}Cu_{20}Fe_{15}$ and Al_7Cu_2Fe were prepared by arc melting in an argon atmosphere of high-purity elemental constituents. No loss of weight occurred during this process. The ingots were cut into slices and were vacuum annealed at 1000 K for 48 h. The $Al_{65}Cu_{20}Fe_{15}$ sample used in this work was the same as the one used in our earlier study.[36] The ribbons produced by melt spinning were not used in this study as they are very brittle and therefore not suitable for surface cleaning by scraping. The surface cleaning by argon sputtering was not used in this work as this may change the sample surface composition.

X-ray-diffraction (XRD) measurements on powder obtained from the slices of alloys chosen for photoemission spectroscopy (PES) studies were performed on a Siemens D500 scanning diffractometer using Cu $K\alpha$ radiation. Before the analysis of the XRD spectra, the contribution from the Cu $K\alpha_2$ radiation was subtracted.

PES experiments were carried out on beamline U14A at the National Synchrotron 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 checked by monitoring the Al 2p line, as discussed in the next section. 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. The position of the Fermi level used as the energy reference in all the spectra was determined with an accuracy of 0.05 eV by measuring the Fermi edge and the Al 2p line (for photon energies 100 eV and higher) of an adjacent Al sample.

III. RESULTS AND DISCUSSION

The XRD lines of thermodynamically stable $Al_{65}Cu_{20}Fe_{15}$ could be indexed to icosahedral structure,[36] whose "lattice constant" a_R (the edge length of the rhombic dodecahedron cells that make up 3D Penrose tiling[37]) is 4.452(2) Å. This value is the same as that found by Tsai, Inoue, and Masumoto.[38] Only one unidentified low-intensity peak at $Q=1.850$ Å^{-1} [Fig. 1(a) in Ref. 36] could not be assigned to the icosahedral structure. It has been recently demonstrated[39–41] that complete removal of distortions initially present in the *rapidly quenched i* Al-Cu-Fe alloys can be obtained by briefly annealing the ribbons at temperatures above 1000 K (the annealing temperatures cited by different authors are in the range 1023–1100 K).[39–41] We found out that annealing the $Al_{65}Cu_{20}Fe_{15}$ ingot at 1093 K for 48 h leads to a multiphase sample. The annealing of the ingot at 1000 K gives a high-quality thermodynamically stable i $Al_{65}Cu_{20}Fe_{15}$ alloy [Fig. 1(a) in Ref. 36]. This is also confirmed by comparing the full width at half maximum, ΔQ, of the XRD peaks of the i $Al_{65}Cu_{20}Fe_{15}$ sample prepared by melt spinning [Fig. 1(b) in Ref. 36] and by annealing the ingot at 1000 K [Fig. 1(a) in Ref. 36]. For example, the ΔQ value for the (100 000) peak is 0.013 Å^{-1} for the former sample and only 0.008 Å^{-1} for the latter. The corresponding values for the (110 000) peak are 0.015 and 0.007 Å^{-1}. The ΔQ values for our sample are thus close to the smallest values found for the annealed ribbons.[41] Independent evidence for the high quality of the i sample used in this work comes from the susceptibility measurements, which showed that it is diamagnetic.[42] The diamagnetism of high-quality annealed ribbons of i Al-Cu-Fe alloys was later confirmed by others.[40,43] The presence of impurities with localized magnetic moment in our sample (such as, for example, $Al_{13}Fe_4$)[44] would lead to an apparent paramagnetic behavior. Thus it is concluded that the thermodynamically stable i $Al_{65}Cu_{20}Fe_{15}$ sample used here is a high-quality, essentially single-phase i alloy.

All lines present in the XRD pattern of Al_7Cu_2Fe could be indexed on the basis of a tetragonal unit cell. The values of lattice constants, a and c, obtained from a least-squares fit of the observed XRD line positions are, respectively, 6.311(1) and 14.805(7) Å. They compare well with the values of 6.336(1) and 14.870(2) Å reported by Brown and Brown.[45] We thus conclude that the samples studied here are single phase.

Since structures observed in PES spectra of metallic alloys are sometimes due to their unwanted oxidation, we first investigated its influence by measuring the spectra of the studied samples in vacuum of 2×10^{-10} Torr directly after scraping and then after a specific time t that had passed from scraping. One can notice a buildup of a peak approximately 1.4 eV below the Al 2p peak after a relatively short exposure to oxygen and other residual gases present in the experimental chamber [spectrum corresponding to $t=1$ h and 30 min in Fig. 1(a); in the spectra presented below, no smoothing or any other corrections were done and each spectrum has been normalized to give a constant height between the maximum and minimum recorded count]. For a much longer exposure [spectrum corresponding to $t=23$ h and 32 min in Fig. 1(a)], apart from the 1.4 eV feature, there is another feature at around 2.4 eV below the Al 2p peak. The influence of oxygen on the Al 2p line has already been carefully studied.[46] It was found[46] that the peak at

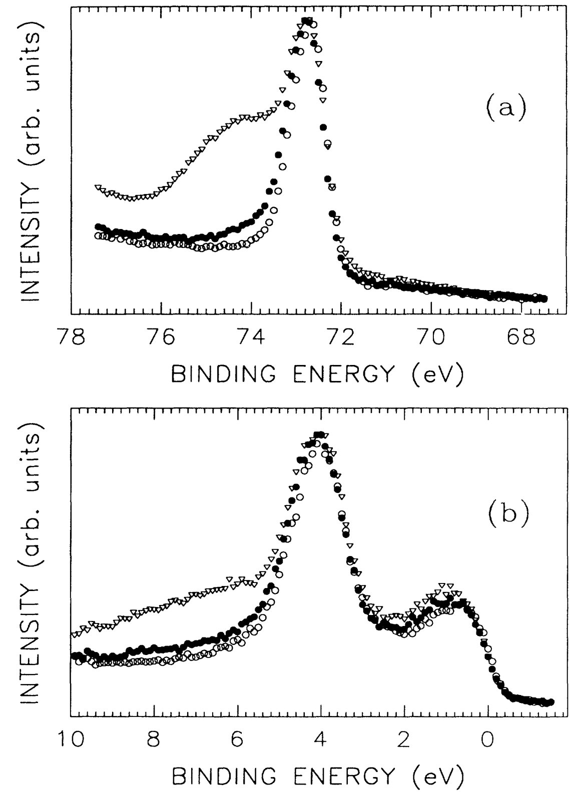

FIG. 1. (a) Al 2p spectra of i $Al_{65}Cu_{20}Fe_{15}$ measured at a photon energy of 100 eV in the vacuum of 2×10^{-10} Torr directly after scraping (○), 1 h and 30 min. (●), 23 h and 32 min. (∇) after scraping. (b) Valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ measured at a photon energy of 100 eV in the vacuum of 2×10^{-10} Torr directly after scraping (○), 2 h (●), and 23 h and 18 min (∇) after scraping.

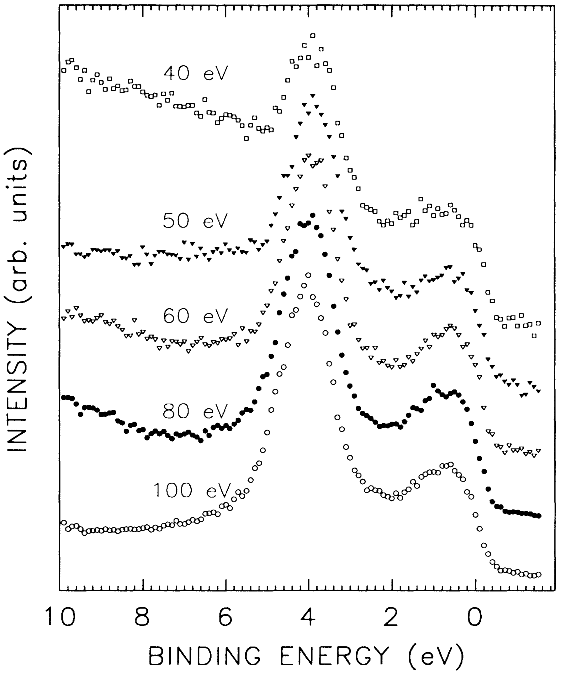

FIG. 2. Valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ excited by photons of different energies.

1.3–1.4 eV below the metallic Al 2p peak is due to chemisorbed oxygen phase, whereas the peak at 2.4–2.6 eV originates from Al in an oxide layer of nearly stoichiometric Al_2O_3. The influence of oxygen and other residual gases can be also observed in the valence-band spectra [Fig. 1(b)]. It manifests itself mainly in a very broad feature at about 7.2 eV below E_F [Fig. 1(b)], which is known[47] to exist when an Al metal is subjected to intermediate exposures of oxygen. The example spectra shown in Fig. 1 enabled us to monitor the state of cleanliness of the sample studied here. It should be emphasized that all the spectra presented in this paper were obtained from at least two different regions of the samples studied, and turned out to be identical. This reproducibility of the spectra additionally confirms the cleanliness of the samples.

Valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ for several photon energies are presented in Fig. 2. Their general characteristics become apparent. First, the overall shape of the valence band does not change very much with the photon energies used. Second, two broad peaks (peak A at about 0.7 eV and peak B at about 4.0 eV below E_F) are clearly exhibited. Third, the intensity at E_F is low.

The origin of various features in a valence band can in principle be identified by the use of tunable synchrotron radiation to observe a resonant photoemission. This is a phenomenon, which was first observed in metallic Ni (Ref. 48) and later in other systems,[49] in which the ionization cross section of an outer-shell electron is enhanced as the excitation photon energy exceeds the threshold of an inner-shell excitation. In transition metals the resonance occurs at excitation energies near the 3p threshold. The Fe $3p\rightarrow3d$ excitation occurs at about 53 eV. Thus, to determine the Fe 3d electron contribution to the features in the valence band of i $Al_{65}Cu_{20}Fe_{15}$ the spectra were measured for photon energies off resonance (below and above 53 eV) and on resonance (at 53 eV). The intensity of the feature A at 0.7 eV (Fig. 3) gradually decreases as the photon energy increases from 50 to 52, reaches its minimum at 53 eV, and then increases for photon energies from 54 to 56 eV. The intensity of the feature B at 4.0 eV (Fig. 3) does not change noticeably with photon energy. We thus conclude that there is a significant contribution from the Fe 3d electrons to feature A of the valence band.

We could not use the Cu $3p\rightarrow3d$ excitation to determine the contribution of the Cu 3d electrons to the valence band because of the overlap of the second-order light from the monochromator. However, this contribution can be identified on the basis of available data and the arguments given below. A review of the valence-band spectra of Cu, Cu-Fe, and Al-Cu alloys (see, for example, Fig. 4 in Ref. 50 and Fig. 1 in Ref. 51) shows that the peak B at 4.0 eV in the valence band of i $Al_{65}Cu_{20}Fe_{15}$ (Figs. 2 and 3) is mainly due to the Cu 3d electrons. Tak-

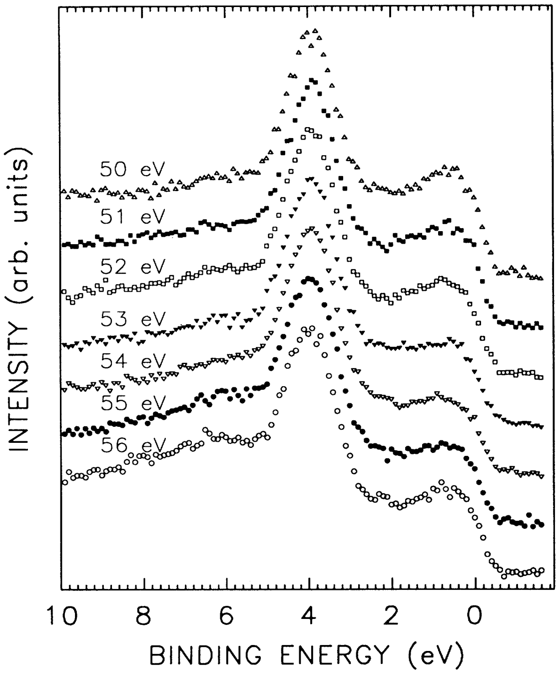

FIG. 3. Valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ for photon energies in the vicinity of the Fe $3p \rightarrow 3d$ excitation region.

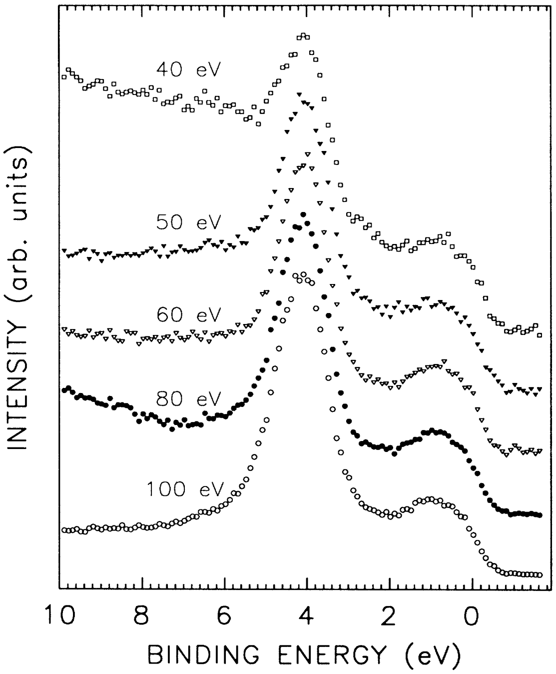

FIG. 4. Valence-band spectra of c Al_7Cu_2Fe excited by photons of different energies.

ing into account the shape of the valence band of Al (Ref. 52) and the fact that the photoionization cross section for Al $3p$ electrons in the photon energy region used here is about two orders of magnitude lower than the cross sections for Cu and Fe $3d$ electrons,[53] one can conclude that the Al $3p$ electrons contribute to the broad plateaulike background onto which the peaks A and B in the valence band of i $Al_{65}Cu_{20}Fe_{15}$ are superimposed.

To determine any difference in the valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ and c Al_7Cu_2Fe, spectra of a c alloy were measured for the same photon energies (Fig. 4) as those of the i alloy (Fig. 2). It is evident from Figs. 2 and 4 that the structure of the valence bands of i $Al_{65}Cu_{20}Fe_{15}$ and c Al_7Cu_2Fe is essentially the same. No unusual features that could be ascribed to the icosahedral symmetry are seen in the valence band of i $Al_{65}Cu_{20}Fe_{15}$ within the resolution of our experiment. The positions of the two major features A and B in the valence bands are essentially the same in both alloys (Figs. 2 and 4).

Valence-band spectra of i $Al_{65}Cu_{20}Fe_{15}$ and c Al_7Cu_2Fe measured at 100 eV photon energy are compared in Fig. 5. It is noticable that they differ only in the intensity of the feature A at 0.7 eV below E_F. This reflects the higher content of Fe in the i alloy than in the c one, and additionally confirms that the feature A is primarily due to Fe $3d$ bands. The similarity of the valence bands of i $Al_{65}Cu_{20}Fe_{15}$ and c Al_7Cu_2Fe (Figs. 2, 4, and 5) indicates that their electronic structure must be very much alike. Within the energy resolution of this experiment, no unusual features in the electronic structure of i $Al_{65}Cu_{20}Fe_{15}$ alloy, which could be associated with the quasiperiodic nature of this alloy, are observed.

Based upon the content of Fe in the studied alloys and the photoionization cross sections (about 4.5 Mb for Fe $3d$ and about 8 Mb for Cu $3d$ for photon energy of 100 eV),[53] one would expect higher intensity of the feature A in the valence band of i $Al_{65}Cu_{20}Fe_{15}$ and c Al_7Cu_2Fe (Fig. 5). The lower intensity of this feature indicates that Fe $3d$ bands, whose contribution to the DOS is largest at 0.7 eV below E_F, must extend to higher binding energies. This observation seems to be consistent with the structure of the experimental valence bands (Ref. 51) and theoretical DOS (Ref. 54) of Fe and Cu, which is more extended to higher binding energies for Fe than for Cu.

The valence-band spectra presented here (Figs. 2, 4, and 5) clearly indicate that DOS (E_F) must be small. The intensity at E_F is slightly smaller for c Al_7Cu_2Fe than for i $Al_{65}Cu_{20}Fe_{15}$ (Fig. 5). However, since the measured PES intensity is proportional not only to DOS but also to other parameters,[55] some of which are virtually impossible to evaluate, it would be difficult to convincingly argue that the slightly smaller intensity at E_F for the c Al_7Cu_2Fe as compared to that for i $Al_{65}Cu_{20}Fe_{15}$ (Fig. 5) corresponds to a smaller DOS (E_F). What one can safely conclude is that the DOS (E_F) in both samples studied are not substantially different.

Although a distinct gaplike structure around E_F is not observed within the experimental energy resolution (Fig. 5), the strong decrease in the DOS towards E_F is indicative that such a structure may exist. The region of unoccupied states above E_F, where one would expect to observe increasing intensity, would have to be measured with an inverse photoemission spectroscopy in order to unambiguously establish the existence of such a

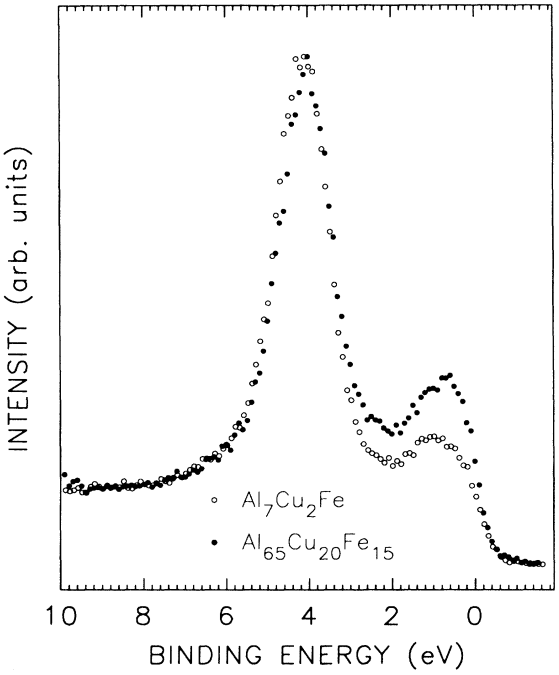

FIG. 5. Valence-band spectra of *i* $Al_{65}Cu_{20}Fe_{15}$ and *c* Al_7Cu_2Fe measured at a photon energy of 100 eV.

structure-induced minimum in the DOS (E_F). We conclude that the strong decrease of the DOS towards E_F in the both alloys studied is suggestive of the existence of a pseudogap in the DOS at E_F. This is consistent with the theoretical predictions[14–16] and constitutes one of the factors determining the stability of the *i* Al-Cu-Fe alloys. Thus, both the *i* $Al_{65}Cu_{20}Fe_{15}$ and *c* Al_7Cu_2Fe alloys can be regarded as Hume-Rothery type of alloys.

We observed no shifts in binding energy of the Al 2*p* line and of the features *A* and *B* in valence bands between *i* $Al_{65}Cu_{20}Fe_{15}$ and *c* Al_7Cu_2Fe. This agrees with SXE and x-ray photoelectron spectroscopy experimental results,[33,34] and is at variance with the theoretical prediction of McHenry *et al.*[8] of a large shift.

The identical structure of valence bands of *i* $Al_{65}Cu_{20}Fe^{15}$ and *c* Al_7Cu_2Fe alloys (Fig. 5) strongly suggests the similarity of their local crystal structures. Our result may thus be interpreted as an indirect supportive argument for a structural model of *i* $Al_{65}Cu_{20}Fe_{15}$ suggested by Phillips and Rabe.[56] In order to explain transport anomalies in stable *i* alloys Al-Cu-*M* (M = Fe, Ru, and Os), these authors suggested that the internal structure of these alloys is based upon two large building blocks. In particular, they assumed that in the case of *i* $Al_{65}Cu_{20}Fe_{15}$ the first block is the icosahedral one and has electronic properties similar to *s-p* type (free-electron-like) *i* alloys, whereas the second block is derived from *c* Al_7Cu_2Fe. One can thus speculate that the contribution of the first block to the valence band of *i* $Al_{65}Cu_{20}Fe_{15}$ would be in the form of a free-electron featureless band and that the features in the valence band should be mainly determined by the structure of the valence band of *c* Al_7Cu_2Fe, which is what is observed (Fig. 5).

IV. SUMMARY

A review of theoretical calculations and experimental results pertinent to the electronic structure of *i* alloys has been presented. Valence bands of single phase, stable *i* $Al_{65}Cu_{20}Fe_{15}$ alloy and its *c* counterpart Al_7Cu_2Fe have been measured with synchrotron radiation in the photon energy range 40–160 eV. The structure of valence bands is essentially identical in both alloys and does not depend on the photon energy. No unusual features in the valence band of *i* $Al_{65}Cu_{20}Fe_{15}$ alloy, which could be ascribed to icosahedral symmetry, have been detected within the energy resolution of the experiment. The feature of 0.7 eV below E_F has been identified, by using resonant photoemission near the Fe 3*p* threshold, as being mainly due to Fe 3*d* states. The feature at 4.0 eV has been shown to be derived mainly from Cu 3*d* states. The strong decrease of intensity towards E_F was interpreted as evidence for the presence of the minimum of DOS (E_F). It has been argued that the similarity of the electronic structure of the alloys studied here supports a recently suggested two-block structural model of the *i* $Al_{65}Cu_{20}Fe_{15}$ alloy.

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