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LETTER TO THE EDITOR

Resonant photoemission study of the Al-Cu-Fe icosahedral phase

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Abstract. Photoemission spectra of the valence band in an Al-Cu-Fe icosahedral phase are studied at excitation photon energies near the Fe threshold. The constant-initial-state spectra in the binding energy region between 0–2 eV show a resonant characteristic. The spectrum has an asymmetric shape, in which the weak peak is on the lower photon energy side and the strong dip is on the higher side. Its resonant energy seems to be slightly smaller than the 3p–3d core excitation energy of an Fe natural form. The Fe 3d bands are located in the region ranging from E_F to 2–2.5 eV below it, with the maximum contribution at around 0.7 eV binding energy. The smaller binding energy of Fe 3d bands suggests that Fe atoms have small numbers of extra electrons transferred from the other elements. The smaller binding energy (corresponding exactly to Fe 3d states sitting just below E_F) is consistent with Friedel's suggestion that the stability of the icosahedral phase is enhanced by a crossing effect of the 3d states with a nearly free electron-like state below E_F which enhances the energy gap of the Brillouin zone.

The discovery of an icosahedral phase in Al-Mn alloys [1], subsequently observed in many other alloys [2], has caused great surprise due to the combination of crystallographically forbidden symmetry and sharp diffraction spots. However, the arrangement of the atoms in the icosahedral phase has still not been determined because its state differs from the ordinary crystalline state in lattice periodicity. Nevertheless, there has been increasing interest in the electronic properties of icosahedral materials. The anomalous diffraction pattern observed in the icosahedral materials suggests that the electrons are strongly scattered and perhaps have a more or less localized character.

It is known that the Al-Cu-Fe alloy system has a stable icosahedral phase with better quasicrystalline quality [3, 4]. Two remarkable magnetic properties have been found in the icosahedral phase. One is that the magnetic susceptibility is proportional to T^2 . Interpretation of this temperature dependence of Pauli paramagnetism suggests the existence of a sharp dip in the electronic density of states (DOS) at the Fermi energy (E_F) caused by the energy gap of the Brillouin zone [4, 5]. The other property is that the Fe

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atoms do not have localized magnetic moments [5, 6]. The low-temperature specific heat study has given a small DOS at E_F for the icosahedral phase [7], which is consistent with the dip structure. Friedel pointed out the possibility that the dip-like structure can be enhanced by a crossing effect of the 3d states with the nearly free electron-like state with energy slightly below E_F , and that the stability would be augmented in the Al-Cu-Fe icosahedral phase by the increased energy gap [8]. Very recently, a dip-like anomaly in the DOS structure near E_F was confirmed by a photoemission experiment. The width and the depth of the dip were estimated to be approximately 0.35 eV and 70% of a normal DOS, respectively [9]. Surprisingly, these values measured with this 'high energy' UPS study are quantitatively consistent with the values obtained from the results of the two above-mentioned 'low energy' experimental studies. However, the UPS study has left Friedel's suggestion about the role of the Fe 3d states unclear. A qualitatively similar result has been reported in a UPS study on the Al-Cu-Li icosahedral phase [10].

For many transition metal compounds a resonant photoemission study has been a useful tool for obtaining direct information on a partial DOS of each constituent element [11]. The principal purpose of this study is to observe resonant photoemission in the Al-Cu-Fe icosahedral phase, find the Fe 3d emission and discuss the relation between the result and Friedel's suggestion about the role of the Fe 3d states on the stability of the icosahedral phase.

The sample used in this study—an $\text{Al}_{65}\text{Cu}_{21}\text{Fe}_{14}$ icosahedral-phase alloy—was a polyquasicrystalline ingot prepared and checked by the same method as reported previously [9]. Photoemission studies were performed at beam line 8B2 of the UVSOR synchrotron radiation facility at the Institute for Molecular Science. All measurements were carried out at room temperature. The analyser resolution was about 0.3 eV at a photon energy of 40 eV, defined by the width of a Gaussian-shaped function. The specimen was very brittle, so clean surfaces were obtained easily by scraping with a diamond file in a vacuum of 3×10^{-8} – 7×10^{-8} Pa. The same was then immediately transferred to the UPS experimental chamber and measured in a vacuum of 0.5×10^{-8} – 3×10^{-8} Pa. This pressure was enough to study the photoemission measurement for several hours [9]. A spectral dependence of incident radiation on the specimens was determined from the photoelectric yield spectrum of gold.

Figure 1 shows energy distribution curves (EDC) of the Al-Cu-Fe icosahedral phase for various excitation photon energies near the Fe 3p core threshold. The EDC intensity is normalized with respect to the synchrotron electron current. These curves keep almost the same shape independently of the incident photon energy [9]. The strong peak observed at the binding energy of 4.1 eV seems to originate mainly from 3d bands of Cu atoms. This binding energy (4.1 eV) is almost the same as the binding energy (4.5 eV) of 3d states of Cu atoms given by an XPS study of Al-rich Al-Cu alloys [12]. A small bump, the maximum of which is observed at a binding energy between 0.6 and 0.8 eV, seems to originate mainly from 3d bands of Fe atoms. This energy (0.6–0.8 eV) is considerably smaller than the binding energy (1.2 eV) of 3d states of Fe atoms given by an XPS study of Al-rich Al-Fe alloys, which clearly showed the Fe 3d peak [12]. This peak is too small in spite of the fact that the sample contains 14 at. % Fe. It is, however, not clear whether this estimated value of the maximum of the Fe 3d bands is the true binding energy or not, because the energy position is very near E_F .

A small change in the EDC of the Al-Cu-Fe icosahedral phase could be observed for the incident photon energy near the 3p-excitation threshold energy of 53 eV for Fe (figure 1). It is well known that the Fe 3d cross section increases resonantly at photon energies corresponding to the Fe 3p core excitation. The width of the Fe 3d bands can

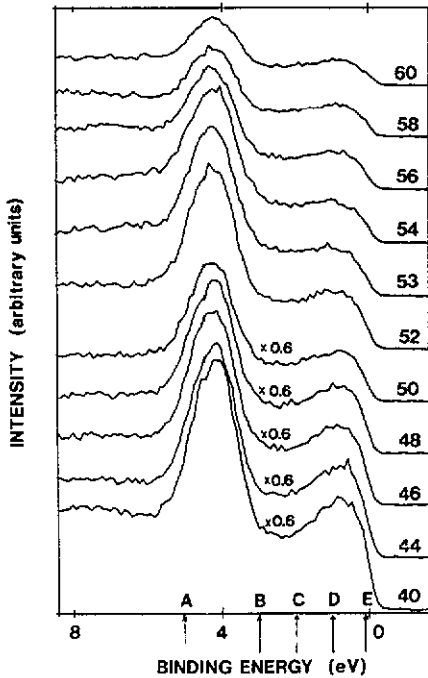


Figure 1. Photoemission spectra of an Al-Cu-Fe icosahedral-phase alloy measured at room temperature for various incident photon energies, the values of which are shown in eV for each spectrum. The intensity of the spectrum is scaled down by 0.6 for incident photon energies under 50 eV.

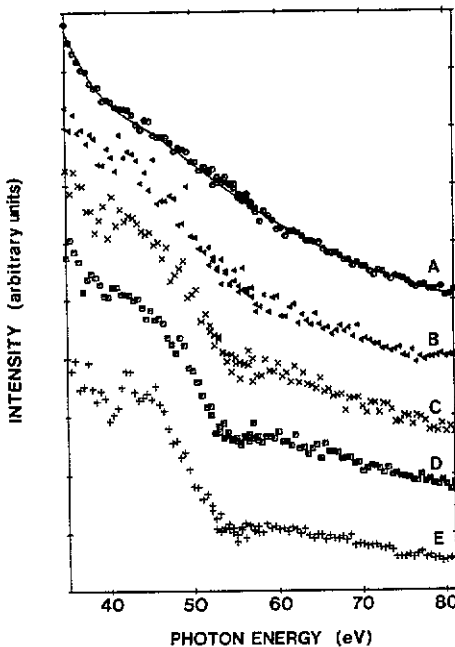


Figure 2. CIS spectra of the Al-Cu-Fe icosahedral phase at room temperature for several binding energies. A, B, C, D and E correspond to the spectra at binding energies of 5.0, 3.0, 2.0, 1.0 and 0.1 eV, respectively. These positions are shown in figure 1.

be estimated using such a resonant phenomenon. The constant initial state (CIS) spectra [13] (with the initial state at several binding energies) were measured at room temperature (figure 2). The CIS spectra A and B in figure 2 do not show a remarkable

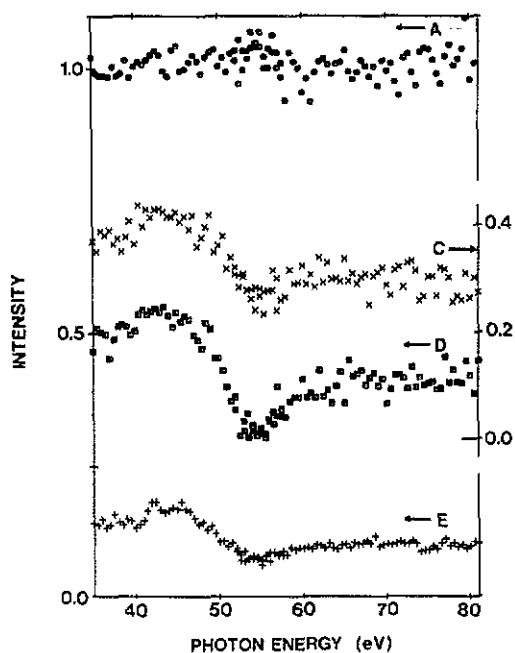


Figure 3. Relative CIS spectra of the Al-Cu-Fe icosahedral phase at room temperature for several binding energies. The spectra A, C, D and E represent the CIS spectra of A, C, D and E divided by the fitted spectrum, respectively. The definitions of A, C, D and E are the same as in figure 2.

resonance effect in the region of the observed photon energy. Therefore, the electron states at positions A and B can be assigned to the states which are non-hybridized with Fe 3d orbitals and which consist mainly of contributions from Al and Cu components. On the other hand, an 'anti-resonant' dip is observed in spectra D and E in the region of the Fe 3p-3d core excitation energy. The electron states at these energies can be assigned to be the states which are hybridized with the Fe 3d orbitals and which contain appreciable amounts of Fe 3d electrons. Spectrum C shows a small 'anti-resonant' dip in the region of the Fe 3p-3d core excitation energy. The electron states with a binding energy of 2 eV are assigned to be the states which are hybridized with the Fe 3d orbitals and which contain small amounts of the Fe 3d component. The result leads to the interpretation that the Fe 3d bands are located in the region ranging from E_F to a binding energy of 2-2.5 eV, with the maximum contribution at around 0.7 eV. The value estimated from figure 2 is almost the same as that given by the position of the maximum of the small bump shown in figure 1. None of the spectra in figure 2 show any remarkable resonance effect at the photon energy corresponding to the Cu 3p core excitation. This is probably because the 3p-3d transition probability is quite small due to the Cu 3d orbitals being full.

As the intensity of CIS spectra is severely dependent on the incident photon energy, we cannot discuss the detailed resonant feature by using figure 2. The fitted spectrum (full curve A in figure 2) was estimated from the non-resonant spectrum A. The relative spectrum A in figure 3 (defined to be spectrum A in figure 2 divided by the fitted spectrum) indicates the validity of the fitting. The other spectra in figure 3 show the relative CIS curves given by spectra C, D and E (from figure 2) divided by the fitted spectrum. They represent the detailed resonant feature at the corresponding binding energies on this icosahedral specimen. They have essentially the same asymmetric shape, in which the weak peak is on the lower photon energy side and the strong dip is on the

higher side. The resonant feature is not small, taking into account the Fe concentration of the sample. It is slightly difficult to determine the exact resonant energy, which seems to be around 52 eV—slightly less than the 3p–3d core excitation energy (52.7 eV) of an Fe natural atom—but it becomes clear that the true binding energy at the maximum of the Fe 3d DOS is the same (0.6–0.8 eV) as in figure 1. Spectrum B in figure 2, being almost non-resonant, was omitted from figure 3 for simplicity.

The smaller binding energy of Fe 3d bands suggests that Fe atoms have small amounts of extra electrons from the other elements and that the one-electron states are raised by the electron–electron interaction and/or the screening of the ion potential. It also suggests that the sharp dip in the DOS is partially enhanced by the hybridization of Fe 3d states just below E_F so that the Fermi sphere circumscribes the Brillouin zone with an increased energy gap, as pointed out by Friedel [8]. Presuming that the number of extra electrons around the Fe atoms is small, then the case of a larger Fermi radius of 0.2578 \AA^{-1} [5] is more reasonable and favourable in the present model, as Friedel suggested [8]. It is also not inconsistent with the above discussion that the resonant energy seems to be slightly smaller than the 3p–3d core excitation energy of an Fe natural atom.

The presumption that the Fe 3d band is broader than 2 eV suggests two possibilities for the 3d electron state of Fe atoms. One is that the 3d electrons are not localized spatially, like the 3d electron bands in a normal transition metal. Another possibility is that the Fe atoms sit on various inequivalent sites. The binding energy of Fe 3d electrons changes variously with site considering that they may be more, or less, localized. The localized nature of the 3d electrons is inferred from the fact that the icosahedral phase could exist in the proximity of a semiconducting state [14]. Broad quadrupole splitting lines have been observed with ^{57}Fe Mössbauer spectroscopy [6]. The 3d states of Fe atoms are thus concluded to be located below E_F , which is not qualitatively inconsistent with the fact that the Fe atoms have almost no magnetic moments. However, the energy position of the 3d states is rather near E_F , and the validity of the naive interpretation [5] based on Anderson's criterion for local-moment formation seems to have to be examined more quantitatively. More quantitative theoretical investigation would be necessary for a discussion based on the present experimental result.

The feature has an asymmetric shape, in which the weak peak is on the lower photon energy side and the strong dip is on the higher side. The asymmetry is opposite to a useful resonant shape observed in the transition metals [11], but it seems quite probable [15]. The origin of such an asymmetric resonant phenomenon is beyond our consideration.

UPS and CIS studies on the other quasicrystals are needed to investigate the relation between such asymmetry and the intrinsic properties of a quasicrystal.

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