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LETTER TO THE EDITOR

Photoemission study of an Al–Cu–Fe icosahedral phase

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Abstract. Photoemission spectra of the Al–Cu–Fe quasicrystal with the icosahedral phase were studied at room temperature. The line shape of the overall observed spectrum is like a large peak on a plateau cut-off at E_F. The large peak observed at about 4 eV below E_F seems to originate mainly from the 3d state of Cu atoms. The bump was observed at about 1 eV below E_F. The high resolution experiment showed an anomalous valley at E_F in the electronic density of states. This means that the dip at E_F in the DOS has a half-width 0.3–0.4 eV and that its depth is 70% of the value for a no-dip case.

Recently, an Al–Cu–Fe alloy system was found to have a stable i-phase with high quasicrystalline quality [1, 2, 3]. Using this quasicrystal, it was reported that the magnetic susceptibility is proportional to T^2. This fact suggests a sharp dip (valley-like) structure in the electronic density of states (DOS) at the Fermi energy (E_F), since the T^2 dependence occurs due to the Pauli paramagnetism [3, 4]. The dip structure was interpreted in terms of the nearly free-electron-like energy gap inferred from the strong diffraction spots. The existence of such spots may be related to the stability of the i-phase [4]. It was also shown that Fe atoms do not have localized magnetic moments [4]. The study of the specific heat at low temperature indicated that the stable i-phase has a small DOS at E_F [5]. This result is consistent with the existence of the dip structure. Friedel pointed out that the dip-like structure can be enhanced by a crossing effect between the 3d state and the nearly free-electron-like state, and that the stability would be augmented in this Al–Cu–Fe i-phase [6]. Such a small value of DOS at E_F was reported to be observed in even the metastable Al–Mn i-phase by means of an XPS [7]. In this case, the width of the dip-like structure at E_F is not very clear. Such an anomaly corresponding to the well-known dip structure was revealed in the XPS spectra of semimetal solid bismuth [8].

The principal purpose of this letter is the observation of the photoemission electron spectra of Al–Cu–Fe specimens with i-phases. This type of study is important since the data obtained directly explain the electronic structure. The point of interest is the existence of the above-mentioned anomaly in the DOS at E_F.

The sample used in this study, an $Al_{65}Cu_{21}Fe_{14}$ i-phase alloy, was a poly-quasicrystalline ingot prepared by the same method as reported previously [3]. A preliminary check on the quality of the sample was carried out with a Rigaku RAD-2C powder x-ray

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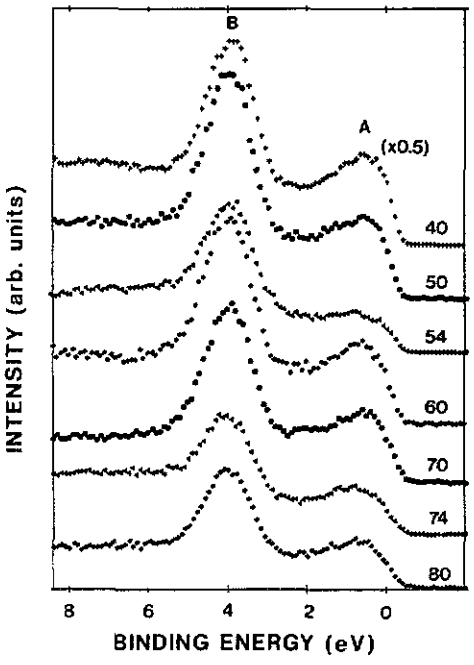

figure 1. Photoemission spectra of the Al–Cu–Fe i-phase alloy measured at room temperature for several incident photon energies. The values of the energy are shown for each spectrum in eV. The intensity of the spectrum is scaled down by a half for the incident photon energy 40 eV.

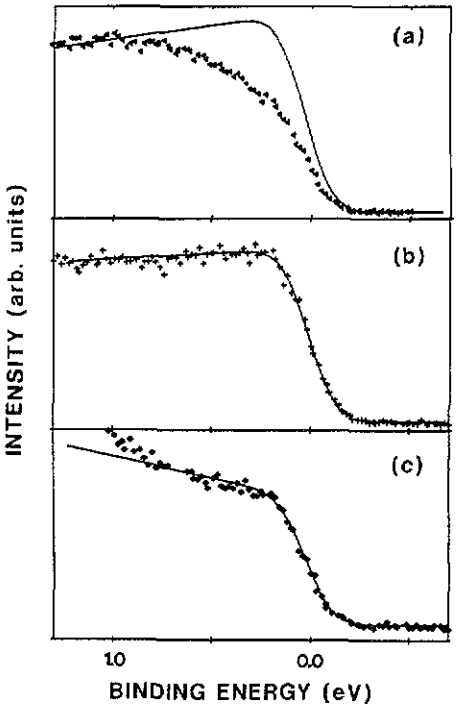

Figure 2. (*a*) Al–Cu–Fe i-phase alloy, (*b*) pure aluminium and (*c*) pure gold. The marked curve is the observed photoemission spectrum near the Fermi edge. All data were obtained by using photons with the energy 40 eV. The full curve is the fitted result assuming that the DOS of the sample is *normal*, except for (*a*). The full curve in (*a*) is calculated with the fitting parameters determined with the data below the binding energy 0.75 eV.

diffractometer. Since the x-ray diffraction pattern was in good agreement with the observed peak intensity map [2], it was confirmed that a large part of the ingot specimen consisted of the i-phase material.

Photoemission studies were performed at beam-line 8B2 of UVSOR in the Institute for Molecular Science. All measurements were carried out at room temperature. The energy resolution could be changed in the range 0.1–0.5 eV in compliance with the experimental aim. The specimen was very brittle; thus, clean surfaces were easily obtained by scraping with a diamond file in a vacuum of $2–5 \times 10^{-10}$ Torr. Immediately after this process, the sample was transferred to the main UPS experimental chamber in a vacuum of $0.4–2 \times 10^{-10}$ Torr. As references, standard spectra of pure aluminium and gold were measured. The pure aluminium sample was an ingot prepared by plasma-jet melting. The pure gold sample was a thin film deposited in the preparation chamber.

Figure 1 shows the photoemission spectra of an Al–Cu–Fe i-phase alloy observed at room temperature with an energy resolution of 0.3 eV. This spectrum keeps almost the same shape against the various incident photon energies. The shape is like a single large peak on a plateau cut-off at E_F. The irregular jump occurring at incident photon energy

between 54 eV and 60 eV is caused by the exchange of the grating operated between these two energy regions. The large peak **B** observed at about 4 eV below E_F seems to originate mainly from the 3d state of Cu atoms according to the XPS results for Al–Cu alloys [9]. Although this sample contains 14 at.% Fe, the clear peak due to the 3d state of Fe atoms was not observed—only a small bump (**A**) was observed at about 1 eV below E_F. Small changes in the spectrum of this i-phase alloy were observed for the incident photon energy across the resonance at the binding energies 75 eV and 77 eV for Cu and 53 eV for Fe. At a glance it seems that the peak **B** resonances occur at 53 eV and the bump **A** at 73 eV. This seems to be contrary to the usual case for resonances of Cu and Fe. A final conclusion about this result will be given after the precise UPS study including CIS experiments.

In order to examine the detailed structure of the DOS (of this i-phase sample) near the Fermi edge, photoemission experiments have been performed under higher resolution (about 0.14 eV = ΔE, defined as the width of the Gaussian distribution function, detailed later) with the incident photon energy 40 eV in its maximal intensity region. The curves made up of marks in figures 2(*a*), (*b*) and (*c*) show the photoemission spectra observed under the resolution (0.14 eV), for the Al–Cu–Fe i-phase, pure aluminium and the gold sample, respectively. While a well-defined E_F is clearly recognized for the pure aluminium and gold (figures 2(*b*) and (*c*)), the spectrum of the Al–Cu–Fe i-phase alloy does not give such a clear Fermi edge (figure 2(*a*)). This phenomenon has qualitatively similar features to solid bismuth which has the well known dip structure [8]. The non-well-defined Fermi edge is usually attributed to the results of adsorbed atoms on the sample in a bad vacuum. In this case, however, the non-well-defined Fermi edge of this spectrum is an *intrinsic* property of this i-phase sample, and is considered to reflect the expected dip structure for the following reasons: (1) the spectrum is reproducible for different samples, and (2) the overall spectrum profile is different from the spectrum of the Al–Cu–Fe i-phase sample covered by the adsorbed atoms. The validity of this fact is also guaranteed by the clear observation of the E_F of pure aluminium oxidized more vigorously.

After assuming that the observed spectrum is proportional to the DOS, a model to reproduce the spectra near E_F is considered, to obtain a quantitative estimation of the dip structure. It is assumed that the DOS near E_F depends linearly on the electronic energy. The DOS of the Al–Cu–Fe i-phase alloy, additionally, has the dip whose shape is assumed to be a Lorentzian function having the centre on E_F and a half width Γ as shown in figure 3(*a*). Thus, an observed intensity $I(E)$ is given by the formula (DOS) $*$ (the Fermi distribution function) convoluted by an energy resolution function (Gaussian distribution type):

$$I(E) = \int (ax + b) * \left(1 - \frac{C\Gamma^2}{(x - E_F)^2 + \Gamma^2}\right) f(x) G \exp(-(x - E)^2/(\Delta E)^2)\, dx$$

where $(ax + b) * \{1 - C\Gamma^2/[(x - E_F)^2 + \Gamma^2]\}$ indicates the DOS at energy x near the E_F with the dip of the DOS near the Fermi edge. In the case of $C = 0$, the system has no anomaly (denoted *normal* DOS), and in the case of $C = 1$, the system has no DOS at the E_F. C is the ratio of dip depth and the *normal* DOS. $f(x)$ and G are the Fermi distribution function at room temperature and a normalization factor of the Gaussian distribution function, respectively. ΔE is the energy width of the Gaussian-type resolution function.

Firstly, the case of $C = 0$ (the *normal* DOS) is considered in order to treat the spectra of pure aluminium and gold. Fitting results, shown as the full curves in figures 2(*b*) and

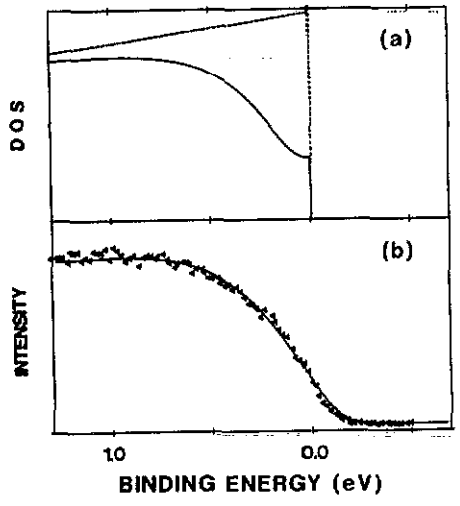

Figure 3. (*a*) The DOS model of the Al–Cu–Fe i-phase for the fitting calculation is made up at $T = 0$ K by subtracting the dip from the *normal* DOS (broken curve). The full curve is for the case of $C = 0.7$ and $\Gamma = 0.35$ eV. (*b*) The marked curve shows the observation data mentioned in figure 2(*a*). The full curve is the fitted result supposing that the DOS of the sample is given in figure 3(*a*).

(*c*), are in good agreement with the observed data using the energy resolution width of $\Delta E = 0.14$ eV and the fitting parameters *a* and *b*. As the calculated curves in figure 2(*a*) do not fit with the observed data, this curve is calculated with the fitting parameters determined with the data between binding energies 1.25 and 0.75 eV. It is noted that the calculated curve drops more abruptly near E_F than the experimental result. Thus, as a next step, the fitting parameter C is introduced to fit the spectrum of the Al–Cu–Fe i-phase sample. The full curve of figure 3(*b*) is the most adequately fitted calculation result using the values $C = 0.7$ and $\Gamma = 0.35$ eV. The dotted curve is the observed spectrum shown in figure 2(*a*). The calculated curve based on the fitting model described above is in good agreement with the observed spectrum. Therefore, it is regarded that this 'dip' model is a good approximation to the real DOS near E_F of this Al–Cu–Fe i-phase specimen.

In summary, a dip-like anomaly was found in the DOS near E_F in this Al–Cu–Fe i-phase alloy with high resolution data. The width Γ of the dip is given as about 0.35 ± 0.05 eV and the DOS on E_F becomes $30 \pm 10\%$ of the *normal* DOS without the dip. These two fitting parameters are strongly correlated with each other. These values should be treated as a rough quantitative guess about the width and the depth of the dip, since an arbitrary assumption of the Lorentzian form is introduced. The model proposed by Matsuo *et al* [3] is supported by the present result. The analysis of the T-dependence of the magnetic susceptibility shows that the half-width of the valley should be at least of the order of 0.3–0.5 eV [10]. The specific heat experiment at low temperature has given a small DOS at E_F, about $\frac{1}{4}$–$\frac{1}{5}$ of the free-electron value [5]. The conclusions of the two independent studies are qualitatively consistent with the present result. The dip structure observed here might be partially enhanced by the effect of the 3d state of Fe as Friedel has suggested [6], and the precise nature of this effect may be worthy of investigation.

Detailed UPS and CIS studies of this i-phase alloy are now in progress. The partial DOS of each component atom is an interesting subject.

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References

[1] Tsai A P, Inoue A and Masumoto T 1987 *Japan. J. Appl. Phys.* **26** L1505
[2] Ishimasa T, Fukanao Y and Tsuchimoro M 1988 *Phil. Mag. Lett.* **58** 157
[3] Matsuo S, Ishimasa T, Nakano H and Fukano Y 1988 *J. Phys. F: Met. Phys.* **18** L175
[4] Matsuo S, Nakano H, Ishimasa T and Fukano Y 1989 *J. Phys.: Condens. Matter* **1** 6893
[5] Wagner J L, Wong K M and Poon S J 1989 *Phys. Rev.* B **39** 8091
[6] Friedel J private communication; 1988 *Helv. Phys. Acta* **61** 538
[7] Traverse A, Dulmoulin L, Belin E and Senemaud C 1988 *Proc. ILL/CODEST Workshop: Quasicrystalline Materials* (Singapore: World Scientific) p 399
[8] Baer Y and Myers H P 1977 *Solid State Commun.* **21** 835
[9] Steiner P, Höchst H, Steffen W and Hufner S 1980 *Z. Phys.* B **38** 191
[10] Matsuo S unpublished