Evidence for the spiky structures in the local density of states of Al-based Quasicrystals

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Abstract

Recent theoretical works have predicted that quasicrystals (QCs) have conspicuous fine electronic structures near the Fermi level (E_F); the density of states (DOS) consists of sharp peaks and deep valleys with several 10meV intervals, which is often called spiky structures. These fine electronic structures are believed to explain the extremely high resistivity of QCs. However, no experiment of observing the fine structures has succeeded for more than ten years. We have investigated the DOS around E_F on icosahedral (i-)AlCuFe, i-AlPdMn, and decagonal (d-)AlCuCo quasicrystals by break junction tunneling spectroscopy at 4.2K and have observed clear peaks of 3.3 $\sim$ 125mV width near E_F. Each peak can be expressed by the probability distribution of the narrow energy gaps that are similar to BCS gaps. This is the first direct experimental result that confirms the predicted spiky structures existing in the vicinity of E_F.

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Quasicrystals (QCs) are a new form of solid states which differs from the other two known forms, crystalline and amorphous. QCs are characterized by possessing a new type of long-range order, quasiperiodicity. The major effort in the theoretical and experimental investigation of the physical properties of QCs has been directed at determining whether quasiperiodicity leads to physical properties which are significantly different from those of crystalline and amorphous materials [1]. The electronic transport properties of QCs are very unusual. A number of Al-based QCs show high electrical resistivity ρ. For example, the resistivity at 4K reaches 10mΩ·cm in icosahedral (i-)QC, and even more than 1Ω·cm in i-AlPdRe QC [2]. Theoretical works have predicted that the density of states (DOS) has two major characteristic features [3]. One is a wide pseudogap of 1eV width at the Fermi level (E_F) in the DOS, the origin of which is due to the *sp-d* hybridization and Brillouin zone - Fermi spheres interaction (the Hume-Rothery mechanism). This wide pseudogap has been observed experimentally by photoemission spectroscopy (PES) [4]. The pseudogap alone, however, could not account for the high resistivity of QCs. The pseudogap is not a unique characteristic feature which distinguishes the electronic structure of QCs from that of crystalline and amorphous alloys, since the pseudogap does occur in both crystalline and amorphous systems. The other feature is unusual peaks and valleys appearing with separations of $10 \sim 50$meV near E_F (spikiness). The presence of the DOS spikiness yields a low group velocity for the electron wave packets that could explain the high resistivity. The spikiness could also explain the unusual sensitivity of the electrical conductivity σ to slight changes in the chemical composition of QCs; such changes shift the position of E_F, which results in a drastic change of the DOS at E_F and, consequently, of σ [5].

The predicted DOS spikiness seems to be a unique property that distinguishes QCs from other materials. The temperature/composition dependences of the electronic resistivity, the thermoelectric power, and nuclear magnetic relaxation times of QCs were interpreted as evidence of the presence of fine structures in the DOS [6–9]. However, the measurements of PES and tunneling spectroscopy (TS), which probe the DOS directly, have not yet been reported to verify this prediction [10–14]. Several reasons have been suggested as to why the TS and PES could not detect the DOS spikiness. The main concern was associated with the fact that the majority of the studied QCs were in a poly-quasicrystalline form; the studied surfaces consist of small poly-quasicrystalline grains with arbitrary orientation which might lead to a smoothing of the existing fine structure of the DOS. In addition, the surfaces are

prepared by *in situ* mechanical scraping and/or cleaving which, in principle, may lead to the destruction of the surface quasicrystallinity. Therefore, spectroscopic measurements with clean and fresh surface of single quasicrystalline samples are essential. A recent theoretical study has reported that the existence of the spikiness is questionable [15], in agreement with the fact that TS and PES could not detect the predicted spikiness. However, it is still believed that a fine structure should exist near E_F because there has been no other appropriate explanation that accounts for the high resistivity and unusual composition dependence of QC properties. In this letter, we report TS with the break junction technique (BJS; break junction spectroscopy) at 4.2K on single *i*-AlCuFe, *i*-AlPdMn, and *d*-AlCuCo QCs, which demonstrates that the predicted spikiness exists in the vicinity of E_F.

The TS technique has the unique capability to probe electronic states. The conductance dI / dV, where I and V are the current and bias voltage across the junction, respectively, is proportional to the DOS, which can be observed through the measurements of $I-V$ characteristics. BJS is one technique of TS. A thin plate of a sample is mounted on the glass-fiber substrate and cracked to form a junction at 4.2K by applying bending force perpendicular to the substrate plane. The measurements were carried out just after cracking the sample. This technique of giving an *in situ* sample-insulator-sample junction is effective for obtaining a clean and fresh interface.

I (V) can be expressed as [16]

$$I(V) = A\,|T|^2 \int_{-\infty}^{\infty} N_{alloy}(E) N_{alloy}(E+eV)[f(E) - f(E+eV)]dE, \qquad (1)$$

where E, $|T|^2$, e and $f(E)$ are the kinetic energy of an electron, the tunneling probability, the charge of an electron and the Fermi distribution function, respectively. A is a constant related to the characteristics of the junction and barrier, and to the velocity of the electrons that pass through the junction. The $N_{alloy}(\ E\ )$ is the DOS of the alloy that forms the junction. The dI/dV was measured at 4.2K by an ac modulation technique with the four-probe method. The junction resistance was 100Ω ~ 100kΩ. Since the tunneling junction of BJS is composed of the same materials on both sides of the barrier, it should give a symmetric spectrum with respect to zero bias (E_F).

Many TS experiments on QCs have been performed by different groups [11–14]. They have confirmed a single sharp dip at E_F as a characteristic feature of the DOS for QCs. Escudero *et al.* have reported several types of structures near E_F in the tunneling spectrum

of i-AlCuFe. One of them showed a peak structure of about 10meV width, which can be related to the spikiness [13]. The structure, however, has been attributed to extrinsic effects because it was not reproducible on i-AlCuFe [14]. Guohong *et al.* observed the fine electronic structures on d-AlCuCo at 2K [17]. However, their spectra did not show any dip at E_F. It was later shown that this was due to the superconducting effects of the counterelectrode [18].

Our BJS measurements were performed at 4.2K with *in situ* cleaving of the sample. The samples used here, namely, i-$Al_{72}Pd_{20}Mn_8$, i-$Al_{64}Cu_{23}Fe_{13}$, and d-$Al_{65}Cu_{15}Co_{20}$, were single QCs of very high quality made by the Czochralski process [19]. It was confirmed by X-ray structural analysis that this i-AlCuFe has an almost perfect i-phase structure [19]. They were cut using a discharge-wire saw into a rectangular shape with the dimensions 2mm x 4mm and 0.5mm thickness. Here, d-AlCuCo is a decagonal QC which possesses a periodic crystalline order along the tenfold axis and a quasiperiodic order in the planes normal to the axis. The electronic properties of d-QCs display anisotropic properties; i.e., metallic behavior is found along the periodic direction while nonmetallic behavior appears in the planes with the quasiperiodic order. The sample of d-QC was cracked perpendicular to the tenfold axis so that the tunneling current along the quasiperiodic direction could be observed.

Figures 1 (a) $\sim$ (c) present the tunneling spectra exhibiting apparent peaks. These spectra show the sharp dip at E_F ($V = 0$) that is a characteristic spectral feature of QCs. The dip structure, however, does not always mean that a characteristic dip exists in the DOS. The dip structure at E_F often appears due to the electron-electron interaction in the TS measurements of QCs [14]. The appearance of a couple of peaks on the shoulder of the dip structure shows that the characteristic dip exists in the DOS [20]. The peak energy corresponds to the energy of the dip edge in the DOS. In Figs. 1(a)$\sim$(c), the reproducible peaks were observed on all measured alloys, i-AlCuFe, d-AlCuCo, and i-AlPdMn. The spectrum in Fig. 1(b) inset, which was measured along the periodic direction of d-QC, is almost constant between -40 and 20mV and shows that the tunneling current obeys Ohm's law. The peak positions in Figs. 1 and 2 are asymmetric with respect to the bias polarity. The asymmetry is attributed to different tunneling processes between opposite biases. The spectrum in Fig. 1(c) shows a parabolic background shape at high bias and a $V^{1/2}$-dependent shape near E_F, which was often observed with another tunneling technique [11–14].

The spectrum with the shoulder peaks of bias separation (V_{p-p}) $\approx$ 290mV is observed in

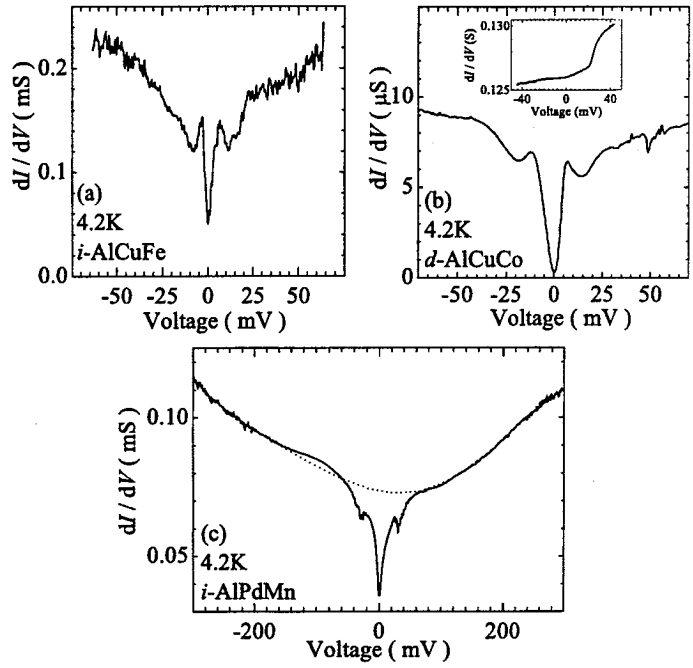

FIG. 1: (a)Tunneling spectrum of *i*-AlCuFe. Clear peaks exist at -3.3 and 6.6mV. (b) d-AlCuCo. Clear peaks exist at -12.0 and 6.6mV. Inset is the spectrum where the current is along the periodic direction. dI / dV is almost constant between -40 and 20mV, which shows the tunneling current obeys Ohm's law. (c) *i*-AlPdMn. Clear peaks exist at ±25mV. Broad humps appear at around ±70mV. The dotted line is the fitted background conductance obtained with a biquadratic function.

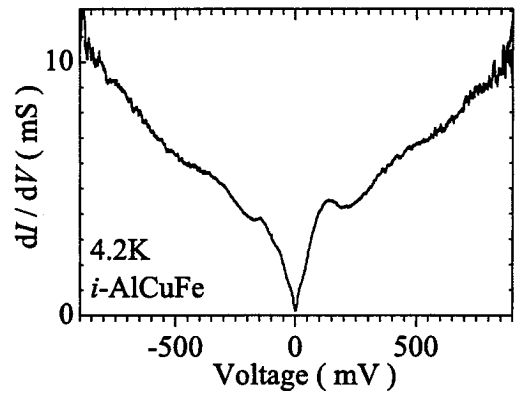

FIG. 2: Tunneling spectrum of *i*-AlCuFe. Clear peaks exist at ±125mV. Clear humps are appeared at around ±400mV. The hums slightly appeared at around ±10mV correspond to the peaks in Fig. 1(a).

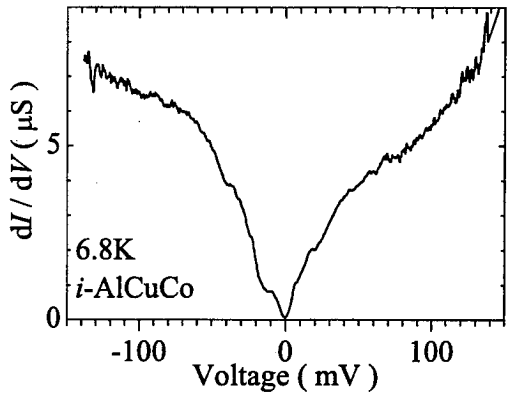

FIG. 3: Tunneling spectrum of d-AlCuCo at 6.8K. Some shoulder structures appear clearly. The bias voltages of humps, -10 and 5mV, correspond to the peaks in Fig. 1(b)

i-AlCuFe, as shown in Fig. 2, in which the V_{p-p} value is an order of magnitude larger than that of in Fig. 1. Such a large peak is observed for the first time by TS. The spectrum in Fig. 2 shows humps in addition to the apparent peaks. The humps slightly appeared at around $\pm$10mV correspond to the peak structure of i-AlCuFe shown in Fig. 1(a). Other humps are seen at around $\pm$400mV ($V_{p-p} \approx$ 800mV). This energy size corresponds to the large pseudogap of the Hume-Rothery mechanism, which is confirmed experimentally by PES [4].

The noteworthy feature of the BJS spectra in Al-based QCs commonly observed in Figs. $1 \sim 2$ is that the pronounced low-energy peaks or humps are concomitant with those of the high-energy ones. This picture coincides with the recent experimental results of thermoelectric properties [21]. The distribution of humps is observed clearly on d-AlCuCo QC, as shown in Fig. 3. The humps of -10 and 5mV in Fig. 3 correspond to the peaks in Fig. 1(b). The humps at $\pm$40mV appeared in both spectra. Therefore, all the humps in Fig. 3 are manifestations of multiple peaks.

Clear peaks such as those seen in Figs. $1 \sim 2$ are similar to those of the gaps of a superconductor or a semiconductor [20, 22, 23]. It is noted that the electronic conductivity of QCs does not decrease between $33 \sim 240$K upon warming [1], although it is expected to decrease at the temperature corresponding to the pseudogap energy. We suggest that the observed peak does reflect the local density of states. The fresh cleavage surface of Al-based single QCs in ultrahigh vacuum is not smooth. It appears as if the surface is composed of bunches of grapes [24]. The grain size of one bunch is evaluated to be about

1nm, which is in good agreement with the size of the fundamental icosahedral cluster of the QCs. This suggests that the intra-cluster bonds are stronger than those between them. The cleavage surface is composed of these clusters, and tunneling occurs between particular atoms located at the top of the clusters. Therefore, the local DOS should be observed. The pseudogap of the local DOS does not indicate the formation of the well-defined pseudogap as the macroscopic property, because pseudogaps of the local DOS are not coherent.

We believe that the BJS technique is suitable for observing the local DOS, allowing for the possibility that the adjacent local density of states is superposed upon the probed tunneling spectra to some extent. We attempt to fit the probability gap-distribution model with the Gaussian distribution function to the spectra in Figs.1(a) and (b), which can provide a picture of the continuously distributed gap values near the junction [20, 25]. In this model, the BCS (Bardeen, Cooper, Schrieffer) density of states is introduced.
The DOS for the Gaussian distribution model, $N_{Gauss}(E)$ is given by

$$N_{Gauss}(E) = \int_{-\infty}^{\infty} \left| \mathrm{Re}\left[\frac{E - \mathrm{i}\gamma}{\sqrt{(E - \mathrm{i}\gamma)^2 - \Delta^2}} \right] \right| \times \frac{1}{\sqrt{2\pi}\delta_0} \exp\left(-\frac{(\Delta - \Delta_0)^2}{2\delta_0^2} \right) \mathrm{d}\Delta \qquad (2)$$

where Δ_0, δ_0 and γ are the mean gap value, the width at half maximum of Δ_0 and the phenomenological broadening parameter, respectively. The experimental spectra were fitted well, as shown in Fig. 4. It is noted that δ_0 is far larger than Δ_0. This is in contrast to the formal assumption that δ_0 should be smaller than Δ_0 in the usual sense of the probability distribution phenomenon. We interpret the meaning of the parameters obtained here as follows. The atomic positions of QCs are not crystallograpiycally equivalent. The DOS of QCs has many different local DOS near E_F, which contribute to the observed tunneling spectra. The coincidence between the Gaussian gap distribution model and the experimental data shows the existence of the dip-edge peak distribution in the QCs. The spectra are composed of the overlapping DOS. In Figs. $1 \sim 2$, the dominant local DOS are observed as peaks and humps, and the other negligible neighboring local DOS merge into the background. In Fig. 3, the superposition of discrete peaks obscure each pronounced peak in the overall conductance. The tunnel barrier characteristics might also affect the conductance feature,

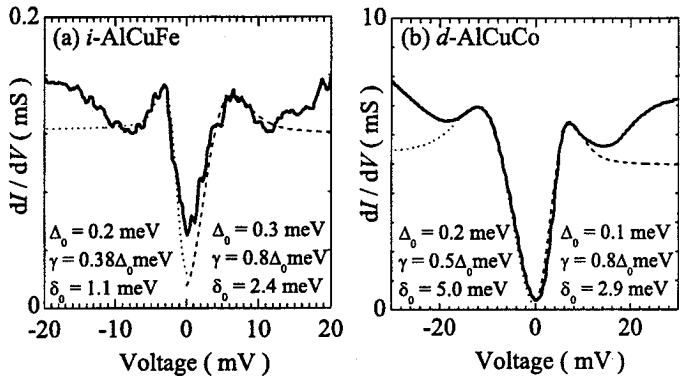

FIG. 4: Fitting of the probability gap-distribution function model with the Gaussian distribution function Eq. (2) to the experimental spectra of (a) i-AlFuFe (Fig. 1(a)) and (b) d-AlCuCo (Fig. 1(b)). Since the experimental spectra are asymmetric, two types of the function were used, as shown by broken and dotted lines. The fitting parameters are shown in the figures.

but the characteristic energy position does not change at all. The interval of the humps is $10 \sim 20$mV, which is in agreement with the interval of the theoretically predicted spikiness. Therefore, we can conclude that the spikiness is observed directly in this work for the first time.

To summarize, we have performed tunneling spectroscopy measurements on i-AlCuFe, i-AlPdMn, and d-AlCuCo QCs using a break junction technique to confirm the existence of fine structures near E_F. Dips of $3.3 \sim 25$mV and 125mV width were clearly observed near E_F for all measured samples. We believe that the low temperature, the fresh surface, and single QCs with a nearly perfect quasiperiodic structure, allow us to measure the peaks and dips clearly. The structures of the peaks and dips are expressed by the probability distribution of the gap. In addition to the apparent peak structures, many hump structures appear. These features may correspond to the variation of the peaks. The energy intervals of the shoulder structures are in agreement with the predicted spikiness. Therefore, it is possible to conclude that the predicted spikiness indeed exists, at least near the Fermi level.

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