Observation of Quasicrystal Surface Order and Disordering by Low-Energy Electron Diffraction

E. G. McRae, R. A. Malic, T. H. Lalonde, F. A. Thiel, H. S. Chen, and A. R. Kortan
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 13 March 1990)

Low-energy electron-diffraction observations indicate the existence of quasicrystalline order at surfaces parallel and perpendicular to the periodic tenfold axis of the decagonal quasicrystal $Al_{65}Cu_{15}Co_{20}$, and of a disordering transition near 715 K at the surface perpendicular to the tenfold axis.

PACS numbers: 61.50.Jr, 61.14.Hg, 68.35.Bs, 68.35.Rh

The structure and physics of quasicrystals are topics of intense and widespread current inquiry.[1,2] These investigations have been limited to the bulk materials, but recently the ability to grow large and nearly perfect samples of decagonal quasicrystals[3] of $Al_{65}Cu_{15}Co_{20}$ has set the stage for studies of quasicrystalline surface ordering as well. Decagonal quasicrystals are of periodic layered structure where the individual layers are perpendicular to the periodic tenfold axis.[4,5] As these layers are thought to be realizations of a two-dimensional quasicrystalline tiling,[6] experimental information about the structure and stability of their surfaces is likely to have an important role in the evaluation of such two-dimensional models. We report low-energy electron-diffraction (LEED) observations of quasicrystalline order at $Al_{65}Cu_{15}Co_{20}$ surfaces respectively parallel and perpendicular to the periodic axis. With reference to the rotational symmetry of the LEED patterns, we call these the twofold and tenfold surfaces, respectively. We report that the tenfold surface undergoes a disordering transition near 715 K, far below the bulk melting temperature about 1280 K,[7] and we briefly discuss the significance of this observation from the standpoint of models of quasicrystalline order and disorder.

The samples used in this work were broken off from a solidified mass consisting of weakly connected columnar grains as previously described.[3] The observation of the twofold surface was made on the as-grown column facet, on which fiber growth lines were visible. The observation of the tenfold surface was made on aligned and polished grains. The samples were mounted in thin-walled (0.002 in.) Ta troughs spot welded to a clip made with a 0.002-in. Ta sheet. The clip was in turn fastened in thermal contact to a 0.02-in.-thick strip of 0.02 Ω cm Si that could be heated Ohmically in vacuum and had a polished (111) surface exposed. A Chromel-Alumel thermocouple was spot welded to the mounting trough behind the sample surface.

The surfaces were prepared by Ne-ion bombardment (7 μA, 800 eV) of the sample and Si support at 650 K, followed by annealing at a higher temperature and cooling to room temperature. Ion bombardment for 3 h, followed by annealing for 1 h at 850 K, resulted in a Si(111)7×7 support surface, and quasicrystal surfaces whose LEED patterns gave clear evidence of quasicrystalline ordering as shown in Fig. 1. The surface impurities determined by Auger-electron spectroscopy (AES) were at levels below 1% of a monolayer (ML) and consisted mainly of C (< 0.01 ML) and O (< 0.002 ML). AES revealed significant surface segregation of Al at

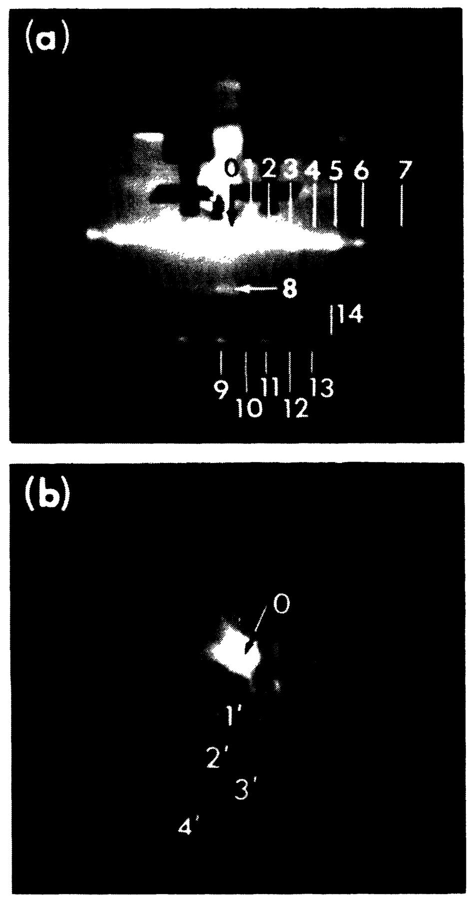

FIG. 1. Room-temperature LEED patterns for decagonal quasicrystal surfaces. Numerals identify the spots whose indices are given in Table I. (a) The twofold surface. Incidence conditions: electron energy $E = 68$ eV, nearly normal incidence. The periodic and quasiperiodic directions are nearly vertical and nearly horizontal, respectively. (b) The tenfold surface. The specular spot is swamped by light from the electron gun. Incidence conditions: $E = 55$ eV, nearly normal incidence. The surface is quasiperiodic in two dimensions.

both the twofold and tenfold surfaces; the surface compositions indicated by sensitivity-weighted AES signals were $Al_{82}Cu_7Co_{11}$ and $Al_{80}Cu_9Co_{11}$, respectively. These results were obtained at each of several sample temperatures ranging from 300 to 800 K after a 1-h anneal at temperature, and also at 600 K after an overnight anneal at temperature.

The LEED patterns were observed using a conventional front-view fluorescent-screen display system. The quasicrystal diffraction patterns were calibrated by comparison with the Si(111)7×7 patterns from the sample support, made under identical incidence conditions. The details of individual spots were observed using a recently developed technique of LEED with position-sensitive detection.[8]

Representative room-temperature LEED patterns for the quasicrystal surfaces are shown in Fig. 1. The spots identified by numerals are indexed in Table I using the reciprocal-space vectors shown in Fig. 2. With reference to these basic vectors, the twofold and tenfold surfaces are respectively labeled by the surface-normal vectors $(0\bar{1}0010)$ and (000001). The indexing scheme is consistent with that used in the presentation of corresponding x-ray-diffraction results,[3] and the lengths a and c of the basic vectors (Fig. 2) required to fit the spot positions are the same within error (±5%) as the corresponding values from x-ray diffraction, namely, $a = 0.63$ Å^{-1} and $c = 2\pi/d$, where $d = 8.26$ Å is the spacing of quasicrystalline layers.

Observations of LEED spot peak intensity I_P versus sample temperature T (Fig. 3) show that the stability of quasicrystalline ordering at higher T is quite different for the two surfaces studied. When the sample is heated, the intensities of both the specular and nonspecular spots in the LEED pattern for the twofold surface decline like a Debye-Waller factor as illustrated by the straight-line plots in the upper part of Fig. 3. For the tenfold surface the specular spot intensity also has the Debye-Waller T dependence (plot 0 in the lower part of Fig. 3) but as also illustrated (plot 2) the nonspecular spots weaken suddenly with increasing T approaching an apparent critical temperature T_1. The T dependence of the non-

TABLE I. Indices of spots in LEED patterns.

(a) Twofold surface $(0\bar{1}0010)$

Spot[a]	q_1/c [b]	q_2/a [c]	n_1 [d]	n_2	n_3	n_4	n_5	n_6
0	0	0	0	0	0	0	0	0
1	0	τ^{-1}	0	1	0	0	1	0
2	0	1	1	0	0	0	0	0
3	0	τ	0	0	$\bar{1}$	$\bar{1}$	0	0
4	0	$\tau+\tau^{-1}$	0	1	$\bar{1}$	$\bar{1}$	1	0
5	0	τ^2	1	0	$\bar{1}$	$\bar{1}$	0	0
6	0	2τ	0	0	$\bar{2}$	$\bar{2}$	0	0
7	0	τ^3	1	0	$\bar{2}$	$\bar{2}$	0	0
8	1	0	0	0	0	0	0	1
9	2	0	0	0	0	0	0	2
10	2	τ^{-1}	0	1	0	0	1	2
11	2	1	1	0	0	0	0	2
12	2	τ	0	0	$\bar{1}$	$\bar{1}$	0	2
13	2	$\tau+\tau^{-1}$	0	1	$\bar{1}$	$\bar{1}$	1	2
14	2	τ^2	1	0	$\bar{1}$	$\bar{1}$	0	2

(b) Tenfold surface (000001)

Spot[e]	$q_\parallel/a$ [f]	n_1 [d]	n_2	n_3	n_4	n_5	n_6
0	0	0	0	0	0	0	0
1′	τ	0	0	0	1	1	0
2′	τ^2	0	$\bar{1}$	0	1	1	0
3′	$\tau\tau'$	0	$\bar{1}$	$\bar{1}$	1	1	0
4′	τ^3	0	$\bar{1}$	0	2	2	0

[a]See Fig. 1(a).

[b]q_1 denotes the momentum transfer parallel to the tenfold axis, and c denotes the length of the basic vector in that direction.

[c]q_2 denotes the surface-parallel momentum transfer perpendicular to the tenfold axis, a denotes the length of the basic vector in that plane, and τ stands for $2\cos(2\pi/10)$.

[d]The indices $n_1, \ldots, n_6$ are the coefficients of the basic vectors (Fig. 2) in the superposition giving the spot position.

[e]See Fig. 1(b). The indices correspond to the orientation of axes such that the vector $a(0\bar{1}\bar{1}110)$ points downward.

[f]$q_\parallel$ denotes the surface-parallel momentum transfer, and τ' stands for $2\cos(\pi/10)$.

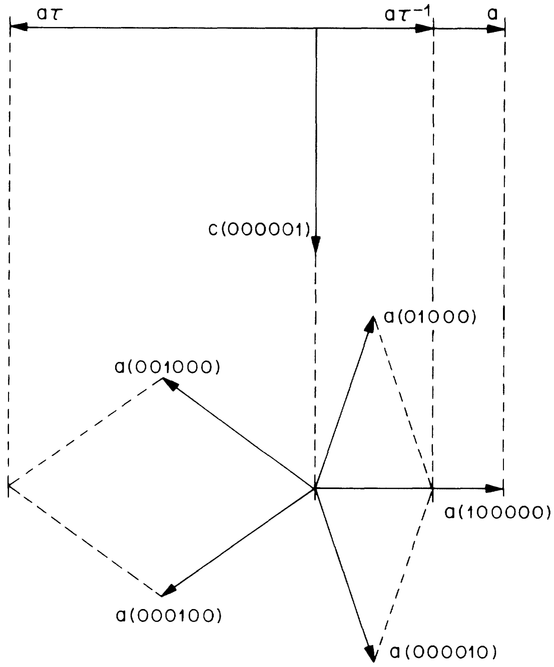

FIG. 2. Basic vectors used in the indexing of the LEED patterns, with illustrative indications of spot positions. The basic vectors comprise the five vectors $a(100000)$,... in the tenfold plane perpendicular to the periodic axis (bottom, plan view of that plane) and the vector $c(000001)$ in the twofold plane parallel to the periodic axis (top, plan view of that plane). The construction (dashed lines) indicates the positions of the first four spots listed in Table I, where $\tau = 2\cos(2\pi/10)$.

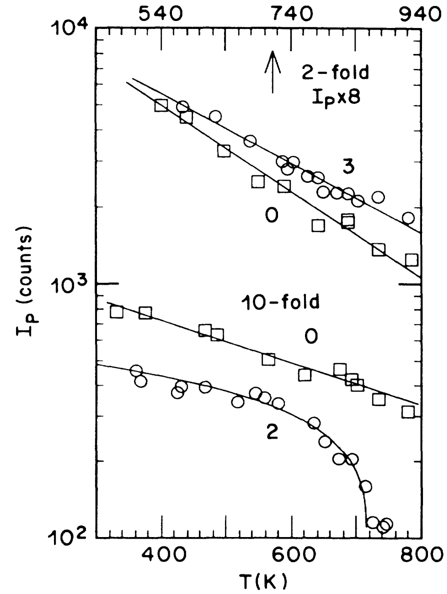

FIG. 3. Dependence of LEED spot peak intensities I_P on sample temperature T. The electron energy was 78 eV. The angle between the incident and reflected beams was 45°. The plots for specular spots are labeled by ○, the other plots by numerals identifying spots in Fig. 1 and Table I. The straight-line fits to the data correspond to the Debye-Waller factor $I_P(T) \propto \exp(-2M'T)$ with the following parameter values: twofold surface, plot 0, $M' = 0.0039\ \mathrm{K}^{-1}$; plot 2, $M' = 0.0031\ \mathrm{K}^{-1}$; tenfold surface, plot 0, $M' = 0.0019\ \mathrm{K}^{-1}$. The fit to plot 3 corresponds to Eq. (1) (see text) with the following parameter values: $\beta = 0.25$, $T_1 = 715$ K.

specular spot intensities $I_P(T < T_1)$ is well represented by an expression of the form

$$I_P(T) - I_P(T_1) \propto (1 - T/T_1)^{2\beta}, \qquad (1)$$

where β is a constant critical exponent. A fit to the experimental points (plot 2, Fig. 3) is obtained with parameter values $\beta = 0.25 \pm 0.02$ and $T_1 = 715 \pm 5$ K. The intensity changes summarized in Fig. 3 were not accompanied by any change of either width or shape of the spot intensity profiles. This is illustrated in Fig. 4, which compares normalized experimental profiles for T respectively above and below T_1. Both sets of experimental data are represented within error by the same profile function—a Lorentzian to the power $\frac{3}{2}$—which is also shown in Fig. 4.[9] Nor were the intensity changes (Fig. 3) appreciably delayed on the time scale of the measurement (100 s at each temperature) regardless of the direction of the temperature change.

We interpret these results as indicating a disordering transition of the tenfold surface at T_1. The interpretation by a surface and not a bulk transition is required to explain the observation of a transition at the tenfold but not at the twofold surface.

With regard to the gross nature of the disordering transition, our observations enable us to make the following points:[10]

(a) In these, as in most other LEED experiments, the surface-normal component to momentum transfer is relatively large compared to the surface-parallel component $q_{\parallel}$, so the results are relatively sensitive to disordering atom displacements normal rather than parallel to the surface plane. Therefore, the fact that the transition affects only the nonspecular spot intensities ($q_{\parallel} \neq 0$) and leaves the specular ones ($q_{\parallel} = 0$) unchanged is an indication that disordering involves atomic displacements primarily parallel to the surface plane.

(b) In view of the high surface sensitivity of LEED, the retention of appreciable nonspecular intensity above T_1 suggests that the disordering displacements are limited to one or at most a few of the outermost atom layers.

(c) The observation of an intensity variation like that of Eq. (1) and the absence of pronounced time delay regardless of the direction of the temperature change are indications that the transition is second order.[11]

The possible mechanisms of disordering transitions at quasicrystal surfaces include the softening of phason modes[12] as well as the surface melting and roughening mechanisms that have been the subject of recent investigations on ordinary crystals.[13]

The softening of phason modes will result in the

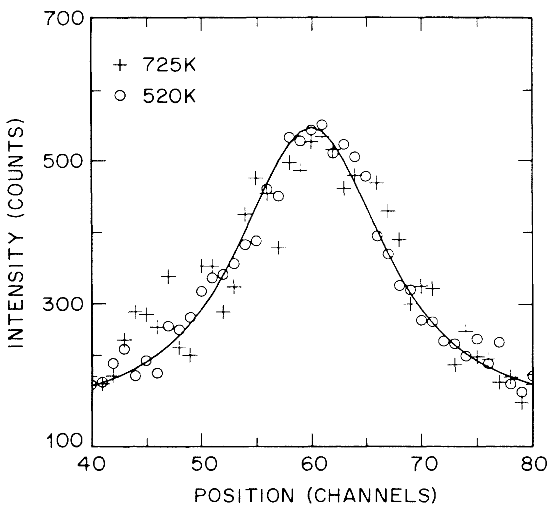

FIG. 4. Experimental spot intensity profiles (data points) for the sample temperatures indicated at top left, and fitted with a Lorentzian to the power $\frac{3}{2}$ (solid curve). The data refer to the tenfold surface, spot 2 [see Fig. 1(b), Table I, (b)]. For experimental conditions see caption of Fig. 3. The 520-K intensity data are output from position-sensitive detector channels on a straight line crossing the spot center. The 725-K data are similar output, normalized to the height of the 520-K profile by subtracting a flat background from the original data, multiplying by 2.55, and adding back the background. The forty-channel width of the plot corresponds to an angular width of detection of 2.2° and a surface-parallel momentum-transfer range of 0.08 Å.

broadening and weakening of different spots to an extent depending on the phason momentum or $G_\perp$,[14] and hence related inversely to the associated values of electron momentum transfer parallel to the surface. A large-area probe like LEED averages over many small regions and the effect of a high density of random isotropic phason density on the diffraction pattern will be a $G_\perp$-dependent peak broadening. Assuming that the total integrated intensity remains constant, peak broadening will also be accompanied by a decrease of the peak intensity. A phason disordering with increasing temperature would therefore have a distinct signature of $G_\perp$-dependent broadening and weakening of the diffraction peaks and different peaks extinguished with different rates. No evidence of these phason-related effects is provided by the present experiments; in particular, no broadening of intensity peaks is observed.

The possibility of roughening was considered in discussions[15,16] of the stability of quasicrystal surfaces. Lipowsky and Henley[15] argued that the tenfold surface of an ideal decagonal quasicrystal should disorder at a lower temperature than a twofold one. Our experiment supports the conclusion that the tenfold surface ordering is relatively unstable, but a roughening mechanism must be ruled out in the present instance because of the observed preponderance of surface-parallel displacements [see point (a) above]. The absence of significant changes of the spot profile is additional evidence against roughening.

[1] *The Physics of Quasicrystals,* edited by P. J. Steinhardt and S. Ostlund (World Scientific, Singapore, 1987).

[2] *Proceedings of the ILL/CODEST Workshop on Quasicrystalline Materials, Grenoble, France, 1988,* edited by Ch. Janot and J. M. Dubois (World Scientific, Singapore, 1988).

[3] A. R. Kortan, F. A. Thiel, H. S. Chen, A. P. Tsai, A. Inoue, and T. Masumoto, Phys. Rev. B **40**, 9397 (1989).

[4] L. Bendersky, Phys. Rev. Lett. **55**, 1461 (1985).

[5] For a review, see S. H. J. Idziak and P. A. Heiney, Philos. Mag. B (to be published).

[6] A. R. Kortan *et al.*, Phys. Rev. Lett. **64**, 200 (1990).

[7] A. R. Kortan, F. A. Thiel, and H. S. Chen (unpublished).

[8] E. G. McRae and R. A. Malic, Phys. Rev. B **42**, 1509 (1990).

[9] In the case of the tenfold surface, an analysis like that of Ref. 8 showed that the profile width and shape parameters defined were independent of T within error bars corresponding to the 95% confidence contour dimensions. The average shape parameter was slightly less than zero, indicating a barely significant pointy-topped character relative to the standard shape (Lorentzian to the power $\frac{3}{2}$).

[10] The properties of LEED underlying the interpretation of the phase transition at the tenfold surface have been explained in detail in a different context: E. G. McRae and R. A. Malic, Phys. Rev. B **38**, 13 163 (1988).

[11] The importance of kinetics in the determination of the order of a surface phase transition has been pointed out in a different context: E. G. McRae, T. M. Buck, R. A. Malic, W. E. Wallace, and J. M. Sanchez (unpublished).

[12] P. A. Bancel, Phys. Rev. Lett. **63**, 2741 (1989).

[13] For a recent example, see H.-N. Yang, T.-M. Lu, and G.-C. Wang, Phys. Rev. Lett. **63**, 1621 (1989).

[14] T. C. Lubensky, J. E. S. Socolar, P. J. Steinhardt, P. A. Bancel, and P. A. Heiney, Phys. Rev. Lett. **57**, 1440 (1986).

[15] R. Lipowsky and C. L. Henley, Phys. Rev. Lett. **60**, 2394 (1988).

[16] B. Yang, W. F. Saam, and J. A. Jaszczak, Phys. Rev. B **40**, 7167 (1989).

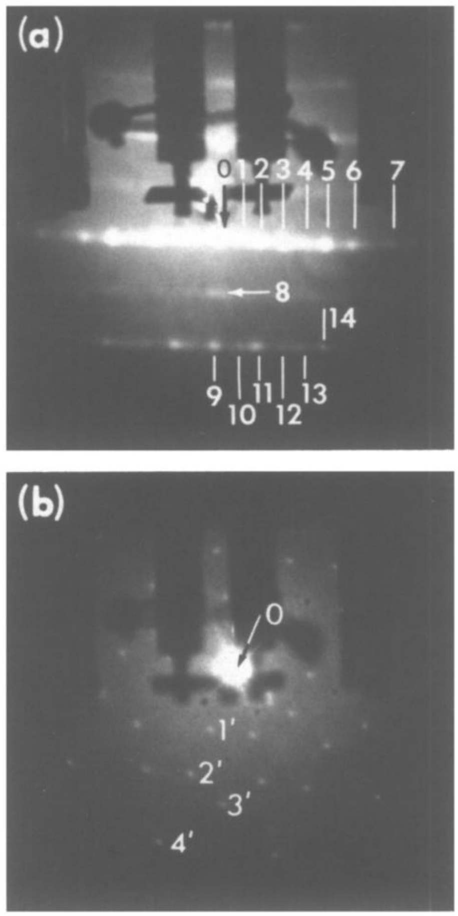

FIG. 1. Room-temperature LEED patterns for decagonal quasicrystal surfaces. Numerals identify the spots whose indices are given in Table I. (a) The twofold surface. Incidence conditions: electron energy $E = 68$ eV, nearly normal incidence. The periodic and quasiperiodic directions are nearly vertical and nearly horizontal, respectively. (b) The tenfold surface. The specular spot is swamped by light from the electron gun. Incidence conditions: $E = 55$ eV, nearly normal incidence. The surface is quasiperiodic in two dimensions.