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Observation of dislocationlike images in large-grain quasicrystals of Li-Cu-Al

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We have observed dislocationlike defect images in a large grain (~1 mm) of Li-Cu-Al quasicrystal which was grown by slow solidification from the melt, followed by heat treatment. Diffraction contrast phenomena, which are common to a crystalline solid, are observed by transmission electron microscopy in this ternary-phase quasicrystal. This observation may lead to a better understanding of the true crystal chemical nature of the quasicrystalline lattice.

Icosahedral quasicrystals generally have a dendritic morphology. It is well known from Al_6Mn quasicrystal that the icosahedral domains (~1 μm in size), when examined in a transmission electron microscope (TEM), exhibit relatively uniform contrast except for the appearance of fine speckles ~200 Å within the domain.[1,2] Diffraction contrast due to local crystal bending and other types of defects such as dislocations, grain boundaries, stacking faults, etc., which are commonly observed in a crystalline material, have not been observed in the icosahedral quasicrystals. Similar defects in quasicrystals, if they exist, would be of great importance to the understanding of mechanical properties of this new class of materials. The absence of these common diffraction contrasts can perhaps be attributed to the overall lattice disorder of the metastable quasicrystalline phase, which was generally obtained by rapid solidification techniques such as melt spinning. Recently, it has been shown[3,4] that the icosahedral quasicrystalline Li-Cu-Al and Li-Cu-Mg-Al alloys can be obtained from classical casting methods and icosahedral grains ~0.1 mm in size were found. The icosahedral quasicrystals in this case were found to be thermodynamically stable and could be formed by solid-state precipitation during annealing at moderate temperatures. However, these quasicrystals still revealed no diffraction contrast phenomena which are common to crystalline materials.

In this paper, we report the observation of dislocation-like line defects, bend contours, and grain boundaries in a very large rain ($\gtrsim$1 mm) of (nominally), $Li_3CuAl_{5.5}$ and of $Li_3CuAl_{5.9}$.

Using the phase diagram of Hardy and Silcock,[5] and some of the preparative data given by Cherkaskin, Kripyakevich, and Oleksiv,[6] we developed a modified process, where experience in other systems has taught us that such changes might enhance the probability of obtaining larger fragments of the desired T_2 phase which has recently been identified as having icosahedral symmetry.[7]

Initially, three melts were prepared with compositions of the following: $Li_3CuAl_{5.9}$, $Li_3CuAl_{5.7}$, and $Li_3CuAl_{5.5}$. The samples with Al nominally 5.5 and 5.9 were those characterized by TEM, with T_2 phase also found in the $Al_{5.7}$ case by x-ray diffraction.

The metals in the crucibles were covered with an eutectic mixture (by wt.%) of LiCl (60%), KCl (40%). An electronically controlled temperature program was started that heated the reactor tube to 800 °C at furnace rate and maintained that temperature for 4 h with Ar flowing. Controlled cooling was then initiated at 3 °C/h and continued at that rate until the temperature reached 460 °C, at which point the temperature was kept constant for 3–4 days. The resultant ingots are approximately 3 cm diam by ~1 cm thick. Excess chlorides are removed by washing the ingots in absolute ethyl alcohol. Water attacks all phases in this region of the phase diagram. Thin-film samples for TEM were prepared by mechanical polishing followed by ion milling.

In Fig. 1, we show selected area diffraction patterns obtained with the zone axis parallel to the fivefold, threefold, and twofold axes of the icosahedral symmetry. The angles between these axes are those expected from the icosahedral $m\bar{3}\bar{5}$ group symmetry. Figure 1 resembles closely those diffraction patterns obtained from the "superlattice" phase of $Al_{74}Si_6Mn_{20}$ quasicrystals.[8] Moreover, many more diffraction spots which were either invisible or very weak in $Al_{74}Si_6Mn_{20}$ now become visible in Fig. 1, suggesting that the icosahedral $Li_3CuAl_{5.5}$ quasicrystal is even more ordered than the Al-Si-Mn quasicrystals.[9] Our electron-diffraction studies indicate that the whole sample (~1 mm in size) is well oriented within a few degrees variation of the symmetry axis. Convergent-beam electron diffraction (CBED), furthermore, reveals

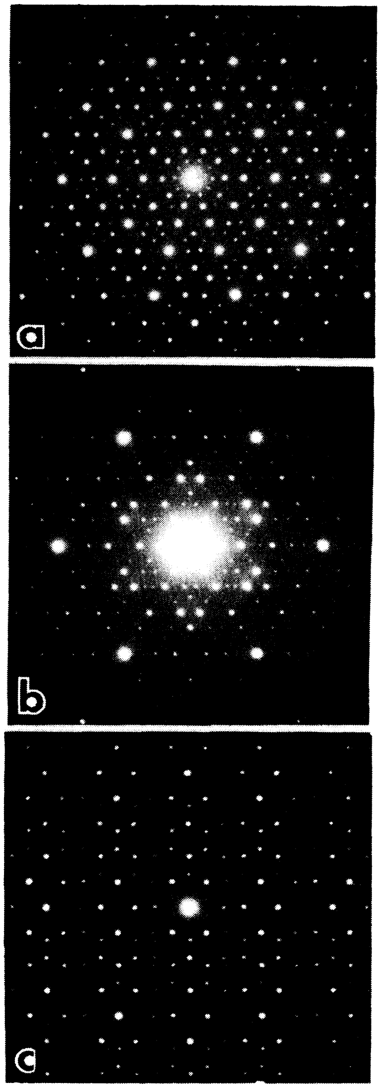

FIG. 1. Electron-diffraction patterns obtained from the icosahedral $Li_3CuAl_{5.5}$ quasicrystal showing (a) fivefold, (b) threefold, and (c) twofold symmetries. Note the elongation of the weak spots especially in the twofold pattern.

that the crystallographic orientation varies slightly over an area of the order of 200 Å.

It is now well known from small area CBED that quasicrystals, strictly speaking, do not exhibit the icosahedral $m\bar{3}\bar{5}$ group symmetry.[10] It was found that the intensities (or the internal structures) of the diffraction disks are not the same among the equivalent disks allowed by the group symmetry. In this case, a CBED pattern was normally obtained by tilting the sample until it yielded the most symmetrical intensity distribution of the diffraction disks. The crystallographic orientation of a chosen small area is thus determined. It is therefore necessary to change the sample orientation slightly each time CBED patterns are taken from various small areas of the sample. It should be noted that this is an intrinsic effect in the quasicrystals and should not be confused with the gradual orientation change due to sample buckling over a much larger scale. We believe that local variation of structural order may be the origin of the intensity variation among the symmetry-equivalent diffraction disks and this variation may not significantly affect the positions of the diffraction disks.

Therefore, strictly speaking, the large grain Li-Cu-Al quasicrystal is not a "single crystal," and should be considered as a phase with mosaic structure. The generalized mosaic structure in quasicrystal does not necessarily imply splitting or streaking of existing diffraction spots, it can also include the intensity variations of the diffraction spots without significantly changing the spot's position. Since x-ray diffraction measurement[4,11] of similar large-grain Li-Cu-Al quasicrystals did not report any splitting or heavy streaking of the diffraction spots, the latter type of mosaic structure must be prevalent. We believe that other Li-Cu-Al quasicrystals reported by other workers have similar mosaic structure. X-ray diffraction measurement[4,11] on these quasicrystals is therefore an average of these mosaic structures and not a "single-crystal" observation.

Examination of the Li-Cu-Al quasicrystals in TEM reveals many types of contrast that are commonly observed in crystalline materials when imaged in so-called two-beam diffraction condition.[12] We show in Fig. 2 both bright and dark field images of an extinction contour due to local crystal bending observed under a two-beam diffraction condition. We note that, to the best of our knowledge, no bend contours have been observed in other

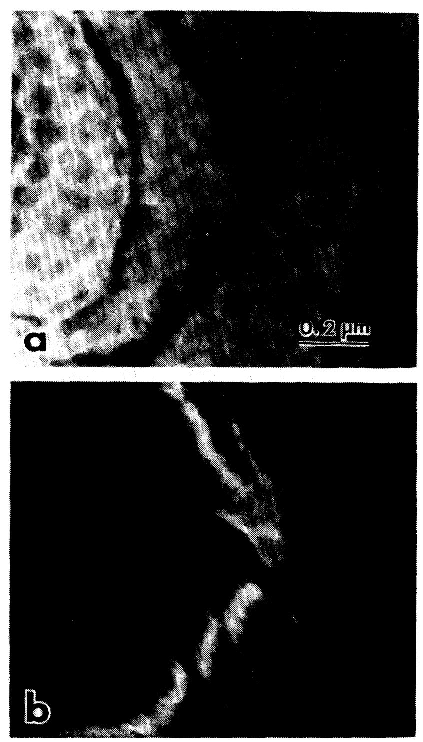

FIG. 2. (a) Bright-field and (b) dark-field images of an extinction bend contour which shifts abruptly at places where dislocationlike line defects are present.

icosahedral quasicrystals. In Fig. 2 we can also see that the excitation contour becomes discontinuous and shifts suddenly at places where dislocationlike defect images are present, indicating that rapid changes in the diffracting condition occur when the dislocationlike defects intersect an extinction contour. In crystalline materials the discontinuous shift of extinction contours across a dislocation is commonly observed in TEM. A pair of bright and dark field two-beam images of these dislocationlike defect images obtained in a thicker region, where extinction contour is not visible, is shown in Fig. 3. The asymmetry of contrast at the line defects is again very similar to that observed at dislocations in a crystalline material. Note that the contrast asymmetry reverses in bright- and dark-field images as would be expected from a dislocation. The contrast asymmetry of the defects in the dark-field images does not appear to change if another diffracted beam is used. We would like to emphasize the long-range nature of the strains associated with these dislocationlike defects, which have been absent in other quasicrystalline systems. It is, however, not clear how defects shown in Figs. 2 and 3 relate to that observed in other quasicrystals by high-resolution electron microscopy, which has shown that lattice planes could suddenly terminate or shift inside the quasicrystals.[13] The length scale of the defects shown in Figs. 2 and 3 appears to be quite unique in all quasicrystals.

Dislocation in a crystalline system is a translational-type defect. Since we are dealing with a system without translational symmetry, the dislocationlike defect images cannot be due to simple dislocations as in crystals. However, considering the quasiperiodic arrangement of structure units in a quasicrystal, it is possible that translational defects can still occur. A row of structural units might be removed (or inserted), and therefore result in changes of the bond orientational order and the coordination number of the icosahedral structural units along the defects. Such a defect is similar to a rotational defect in its effect on the structure, and perhaps we can refer to these defects as disclinations in this case. Disclinations have been used to describe a variety of defects such as dislocations in high-angle grain boundaries,[14] defects in polymers, metallic glasses, liquid crystals, spin systems, etc.[15] Disclinations, like dislocations, have associated stresses and strains[14] that make them readily visible by diffraction contrast in TEM.

Recently, from theoretical considerations, it has been shown that topological defects analogous to dislocations do exist in quasicrystals.[16] It was shown that a Burgers vector **b** can be defined in a six-dimensional lattice within which the quasicrystal can be considered as a regular periodic solid. In a crystalline solid, the Burgers vector **b** can be determined by finding the diffraction spot with reciprocal vector **g** in which the dislocation becomes invisible (i.e., $\mathbf{g}\cdot\mathbf{b}=0$). In quasicrystals, the situation is more complicated and it remains to be seen if the procedure of Burgers vector determination described for crystalline solids will work. We have carried out preliminary two-beam studies of these dislocationlike defects and have not been able to find any systematic extinction conditions for the observed defect images. A detailed diffraction contrast study of the defects is now in progress.

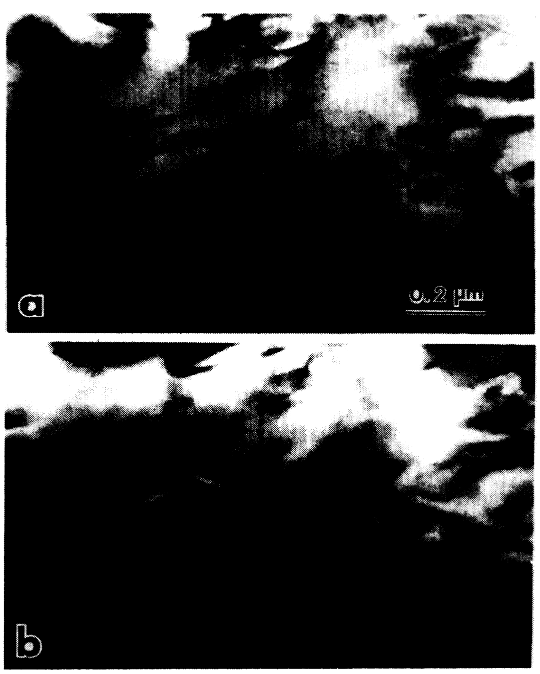

FIG. 3. (a) Bright-field and (b) dark-field images of dislocationlike line defects. Note the asymmetry of the contrast near the line defects and the reversal of contrast of the line defects between (a) and (b).

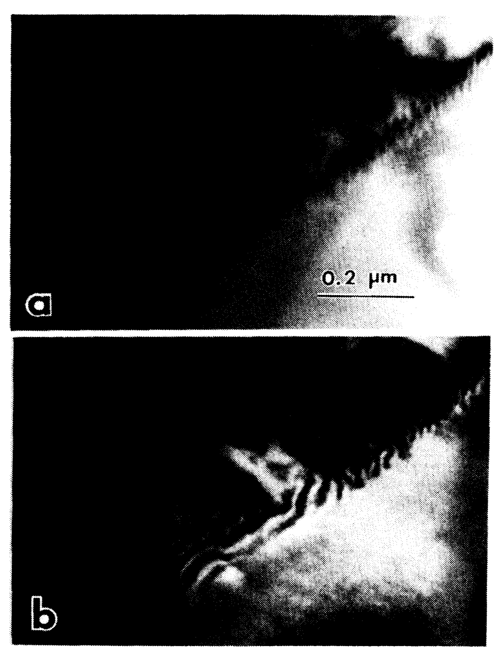

FIG. 4. (a) Bright-field and (b) dark-field images of a grain boundary between two slightly misorientated grains with respect to a common twofold axis approximately perpendicular to the sample surface. Note the regular array of dislocationlike defects especially in the upper half of the boundary.

Occasionally, a well defined boundary due to small orientation difference between two adjacent grains is observed, as shown in Fig. 4. In this particular case, the two grains are misorientated slightly with respect to a common axis approximately perpendicular to the sample surface. The angle of misorientation is estimated to be less than 2° from the accuracy of our electron diffraction pattern. Figures 4 clearly show a regular array of dislocationlike defects at the grain boundary. It is remarkable that this array of defects is very similar to the periodic dislocation array commonly observed at a low angle grain boundary in a crystalline material. It is noted that the orientation and arrangement of the dislocationlike defects in the lower part of the grain boundary have changed, presumably due to change of the grain boundary geometry. In a crystal, the separation of the periodic dislocation l in a low angle symmetric tilt boundary is given by $l=b/\theta$, where θ is the angle of misorientation and **b** is the Burgers vector of the grain boundary dislocation. If we apply this idea to the regular array of dislocationlike defects shown in Fig. 4, we find the Burgers vector is less than 7 Å. The real physical significance of this is not yet completely clear in quasicrystals.

In conclusion, TEM studies have shown the existence of dislocationlike defect images in a large grain Li-Cu-Al quasicrystal. Many different types of diffraction contrast that are commonly seen in crystalline materials are observed in this quasicrystal; however, the detailed nature of the observed contrast are still uncertain. We feel that our observation of dislocationlike defects is a major step forward in understanding the mechanical properties of quasicrystals.

We are indebted to V. Elser and M. Marcus for valuable discussions and initial indexing of all lines in an x-ray powder photo of the T_2 phase, F. J. Sansalone for preparation of TEM samples, and S. N. G. Chu for bringing Ref. 14 to our attention.

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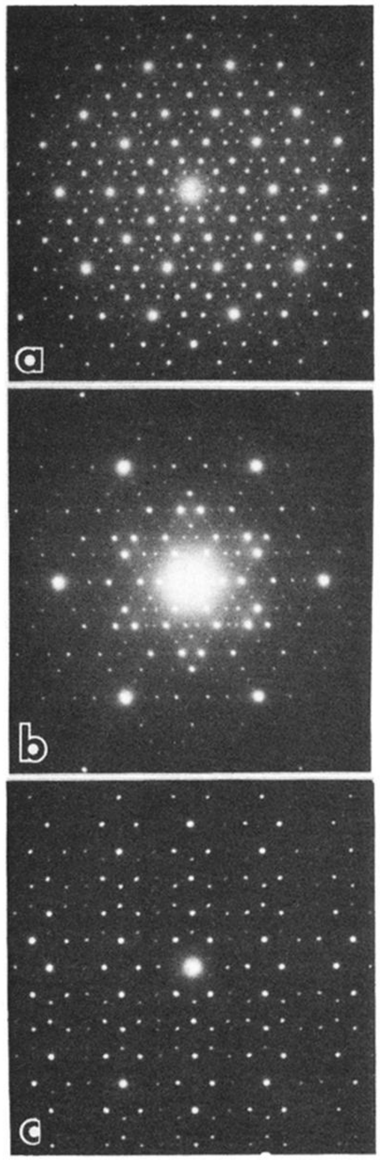

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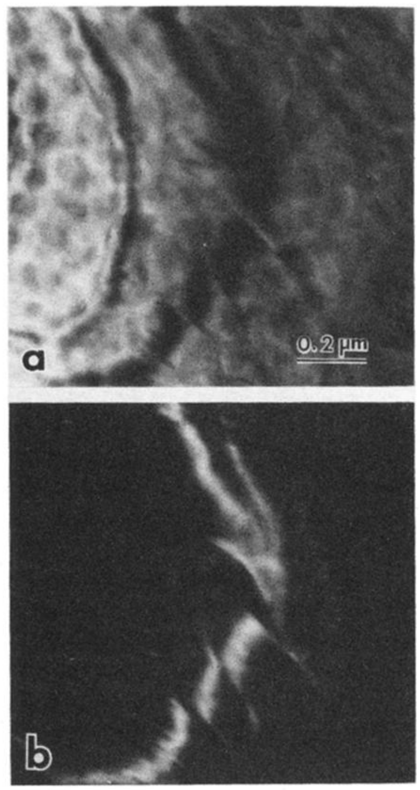

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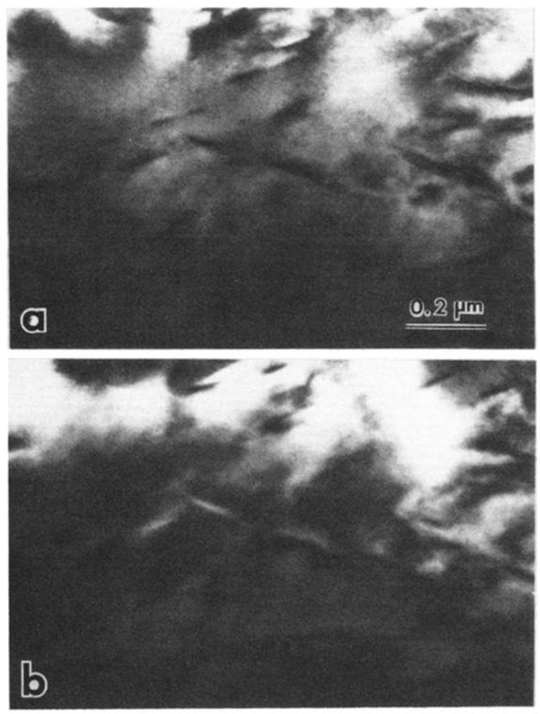

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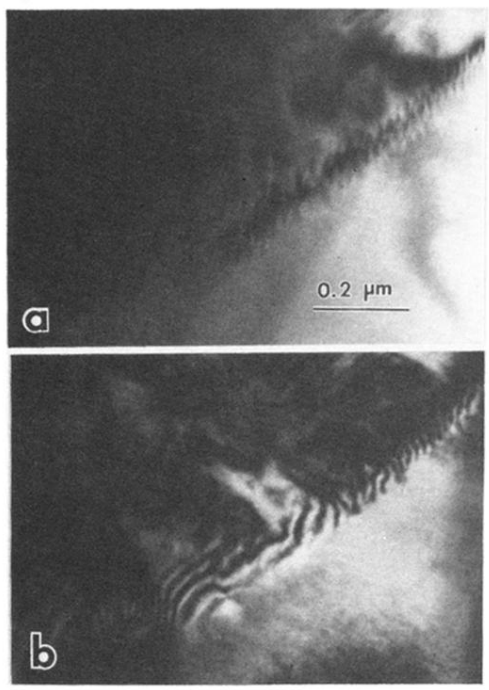

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