Formation of an Icosahedral Phase by Solid-State Reaction

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Icosahedral quasicrystals of Al-Cu-Li are formed by solid-state reaction at the grain boundaries of host alloy. Convergent-beam electron-diffraction measurements confirm that the symmetries of the quasicrystals belong to the $m\overline{3}\overline{5}$ point group. The icosahedral grains are formed by a nucleation and growth process and are strongly oriented at the grain-matrix interface. The stability of the icosahedral phase is compared with that of metallic glasses produced by a similar technique.

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Shechtman *et al.*[1] reported the first experimental example of an icosahedral crystal, one of the new ordered structures known as quasicrystals studied by Levine and Steinhardt.[2] To date, alloys exhibiting icosahedral point-group symmetry are obtained by rapid solidification of the melt,[3–8] by devitrification of the glass,[4,9] and by direct energy processes and interdiffusion of multilayer thin films.[10] From the structural standpoint, the transition sequence melt (glass) → icosahedral solid appears to be favored since finite-range icosahedral orientational order was observed[11] in a molecular-dynamics simulation of a supercooled Lennard-Jones fluid. The stability of icosahedral orientational order in the solidification process has also been discussed by various authors[12–17] using a density wave as order parameter in the Landau free-energy functional mean-field theory. The general conclusion is that the degree of metastability of the icosahedral phase with respect to conventional (simple) cubic structures depends on the choice of input parameters in the calculation. In unravelling the structure of icosahedral Al-Mn alloys, Elser and Henley[18] and Guyot and Audier[19] found similarity in the building blocks of the quasilattice and the lattice of the Frank-Kasper phase. These findings imply that the icosahedral quasicrystalline phase might be quite competitive with respect to crystal phases having complex structures.

We report in this Letter the formation of an icosahedral phase in an Al-Cu-Li alloy by solid-state reaction, but without employment of rapid solidification in the process. Our conclusion is based on high-resolution electron microscopy and convergent-beam electron-diffraction studies. The nucleation and growth of the icosahedral phase is also investigated. A strong orientational relationship between the icosahedral phase and the aluminum matrix is observed. Earlier, Ball and Lloyd[20] reported the presence of intermetallic particles in an overaged Al-Cu-Li-Mg-Zr alloy which showed fivefold symmetry diffraction patterns. Based on the Moiré fringe contrast, they concluded that the patterns had their origin in the twinning of microcrystalline domains.

Solid-solution samples of a conventionally cast Al-Li(9 at.%)-Cu(1 at.%)-Zr(0.05 at.%) alloy, prepared by heat treating the material at 550 °C for 30 min followed by quenching to room temperature, were examined by transmission electron microscopy (TEM). Observations of the solid solution revealed a grain-boundary structure free of second-phase particles [Fig. 1(a)]. Subsequent isothermal treatments in the temperature range between 170 and 520 °C results in the nucleation and growth of particles at grain boundaries which exhibit fivefold diffraction symmetry. The particles are observed to grow along the grain boundary until impingement with other growing particles [Figs. 1(b) and 1(c)], which eventually leads to the complete transformation of the grain-boundary surface to particles. The particles will continue to thicken after 100% impingement and their decomposition into a more stable grain-boundary phase was not observed, even at temperatures approaching the solid-solution solvus (approximately 520 °C). Particle sizes were observed up to ~10 μm in length with thickness of ~3 μm after isothermal transformation times of 24 h at 400 °C.

Selected-area diffraction (SAD) and convergent-beam electron-diffraction (CBED) patterns may be produced for any single particle for fivefold, threefold, and twofold axes which are exactly equivalent to those reported by Schechtman *et al.*[1] for icosahedral-phase particles in Al-Mn alloy (Fig. 2). The angular relationships between these major zones are also consistent with those reported. Energy-dispersive x-ray analysis reveals that the compositional ratio of Al to Cu is ~7:3 with no indication of the presence of Zr.[21] The "quasilattice constant" for icosahedral Al-Cu-Li determined from electron diffraction equals 5.1 Å. This value is similar to the one reported for icosahedral Al-Mg-Zn alloys,[5,8] suggesting that the two alloy systems may belong to the same class of icosahedral crystals.

In order to evaluate the particles for the occurrence of twinned domains, CBED patterns of the fivefold, threefold, and twofold axes were examined for a single particle with an approximate length of 5 μm. In all cases well-developed Kossell-Mollenstedt lines may be seen in the diffraction patterns. This is shown for the fivefold zone-axis pattern in Fig. 3. Analysis of the point symmetry in these patterns revealed the $m\overline{3}\overline{5}$ point group.[22] For a given zone-axis orientation of this particle, a single zone-axis CBED pattern was produced with a spot size down to 20 nm. Furthermore, this same zone-axis pattern was produced regardless of the placement of this spot along the 5-μm length of the particle. If the particles consisted of twinned regions, then the misorientations between twinned domains should be apparent and Kossell-Mollenstedt lines would be absent in the CBED patterns.

Three other observations also provide evidence which would mitigate the occurrence of twinning in these particles:

(1) Structure images produced from beam directions corresponding to the major particle zone axes failed to reveal the presence of twin boundaries. In all cases structure fringes were observed as continuous lines without intersecting boundaries.[23]

(2) In lattice imaging, Moiré fringes were not observed for grain-boundary particles isolated from other particles and the matrix. It was only at regions where particles overlap with the matrix and other particles that Moiré fringes such as those reported by Ball and Lloyd[20] were observed.

(3) For a given orientation of a single particle a series of dark-field images may be produced for any diffracted spot which illuminates the entire particle.[1] Twinned domains or regions are not observed.

The evidence for nucleation and growth of icosahedral phase particles as a solid-state reaction may be derived from experiment:

(1) The icosahedral-phase particles, originally absent from the solution [Fig. 1(a)], are observed to nucleate and grow during isothermal heat treatment in the previously stated temperature range of 170–520 °C.

(2) Dark-field images taken with a 50-μm SAD aperture using a strong icosahedral particle reflection illuminate several particles along a grain boundary [Fig. 1(d)]. Closer examination of each of the particles which are illuminated for a given diffraction condition with CBED reveal that all possess exactly the same orientation with respect to one of the matrix grains. Studying the diffraction patterns taken from different zone axes of the matrix grain reveals that the twofold "atomic planes" (rectangles) in the icosahedral grains are parallel to the aluminum (001)-type

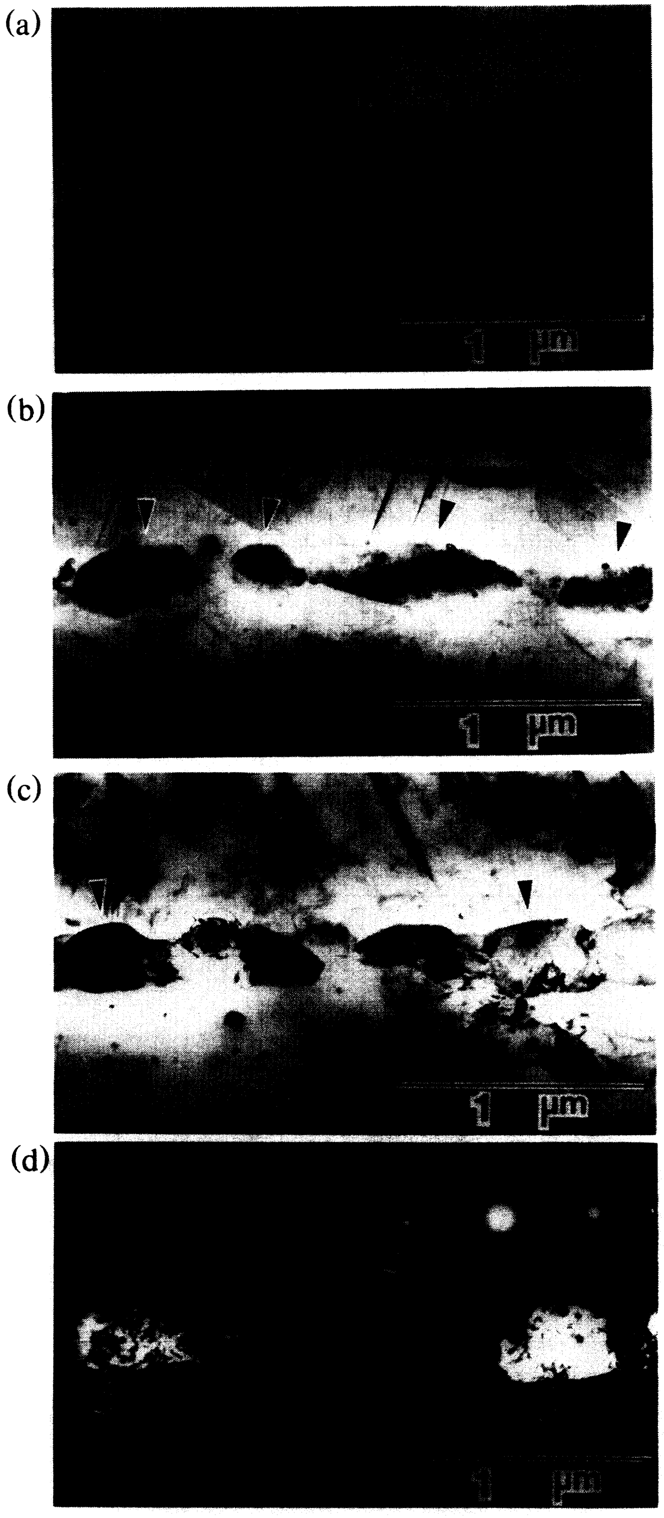
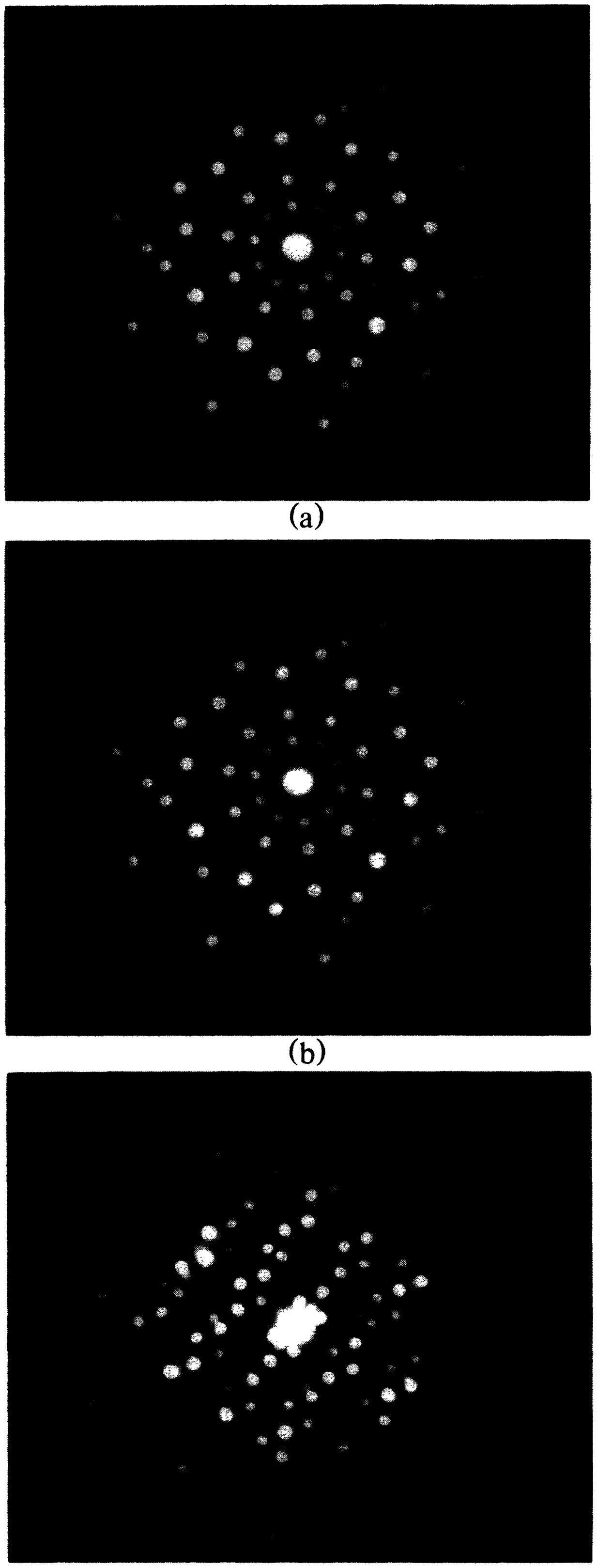


FIG. 1. Transmission electron micrographs for (a) solid solution, 30 min at 550 °C, (b) 6 h at 300 °C, icosahedral particles arrowed, (c) 24 h at 300 °C. (d) Dark-field image corresponding to (c), diffracted spot used arrowed (inset).


(a)

(b)

(c)

FIG. 2. Electron-diffraction patterns for (a) fivefold axis, (b) threefold axis, and (c) twofold axis.

planes (squares) at the interface.[23] A similar orientational relationship was also reported for the Al-Mn system.[24] The edges of the rectangles are rotated away from the edges of the squares by ~31.7°. A strong orientational relationship is expected for a system where second-phase particles are nucleated at a grain boundary in such a way as to minimize its interfacial energy with respect to the two grains. It is important to recognize that the growth morphology is controlled by kinetic considerations which will usually differ from the critical nucleus morphology, which is predominantly controlled by interfacial energy minimization. This process will tend to be reproducible at a given grain boundary [Figs. 1(c) and 1(d)].

The preferential formation of an icosahedral phase in a ternary system by solid-state reaction is rather unusual in view of the abundance of equilibrium phases in the Al-Cu and Al-Li binary systems.[25] Recent results on the synthesis of metallic glasses[26] by solid-state reaction suggest that low temperature suppresses nucleation and growth of equilibrium phases. The glassy phase is therefore preferentially formed because its free energy is lower than that of the starting materials. On the other hand, the peritectic temperatures of Al-Cu and Al-Li intermetallic compounds can be as low as ~580 °C which are within ~100 °C of the temperature at which nucleation and

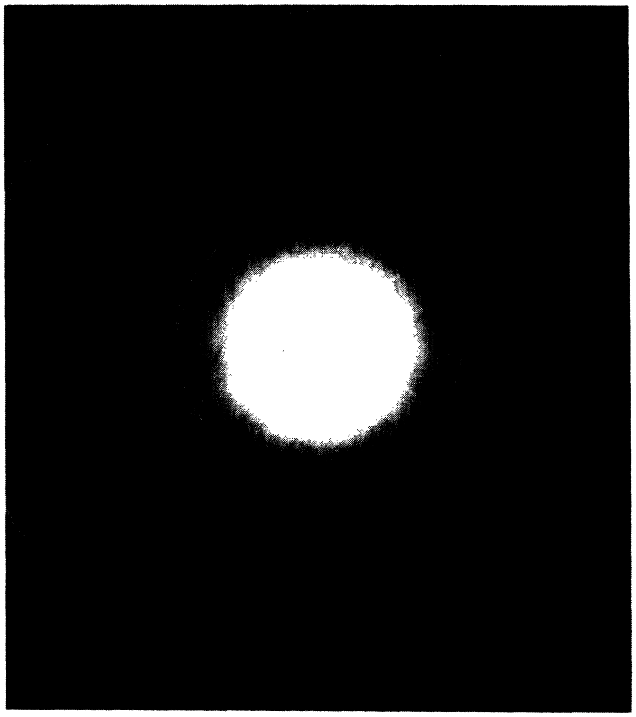


FIG. 3. Convergent-beam electron-diffraction pattern of the fivefold axis showing Kossell-Mollenstedt lines.

growth of the icosahedral phase are still occurring. This shows that the icosahedral phase is energetically competitive with respect to the equilibrium phases whose structures vary in complexity.[25] Recent calculations have shown that the glassy structure is metastable with respect to the quasilattice structure.[15] This would lower the free energy of the icosahedral phase, thus favoring its formation in a solid-state reaction. On the other hand, it has been demonstrated that rapid solidification is required to suppress the formation of the competing Frank-Kasper phases in order to obtain the icosahedral phase.[7,27] The Frank-Kasper–type phases do exist in the Al-Cu-Li system. Thus, the stability of this icosahedral phase deserves further investigation.

Lastly, it should be mentioned that since quasicrystals can be produced by low-temperature solid-state reaction without involving any quenching process, it provides model systems for studying the intrinsic structural and physical properties of this new class of ordered atomic structures.

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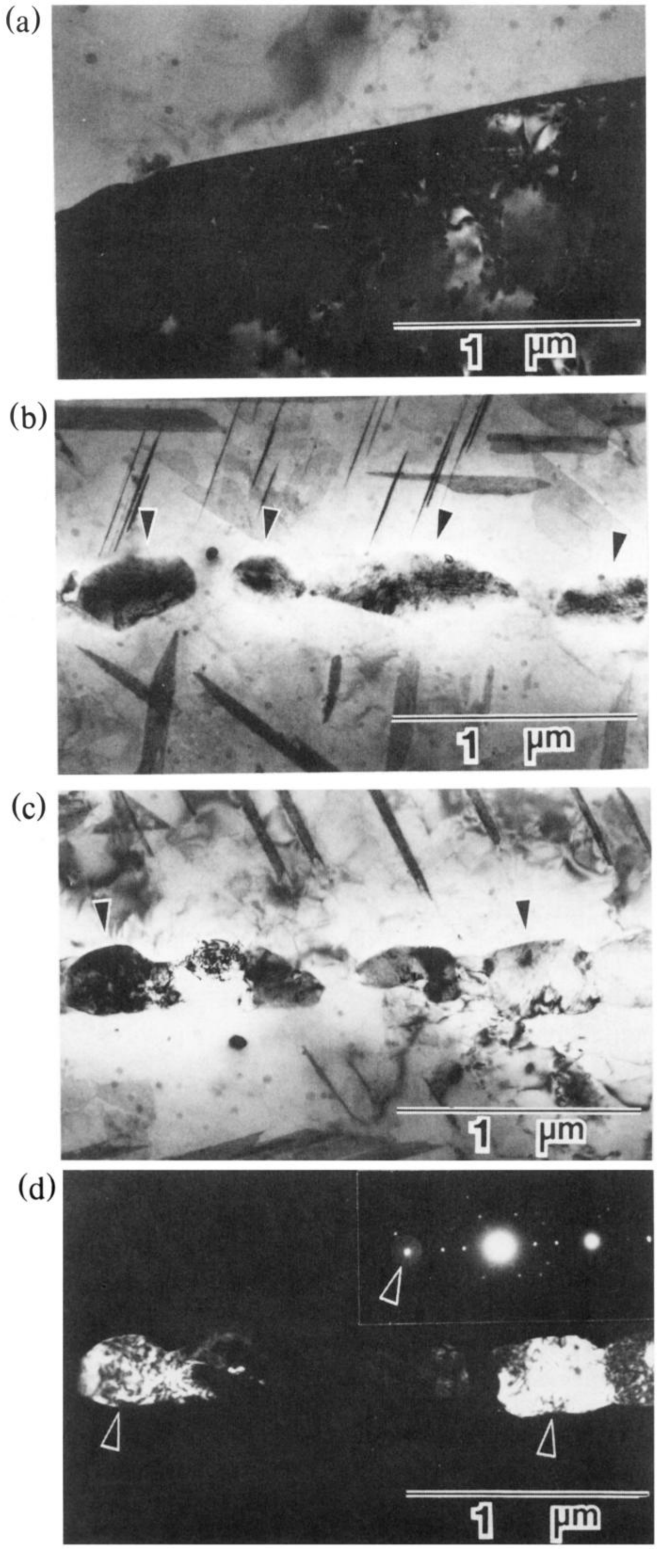

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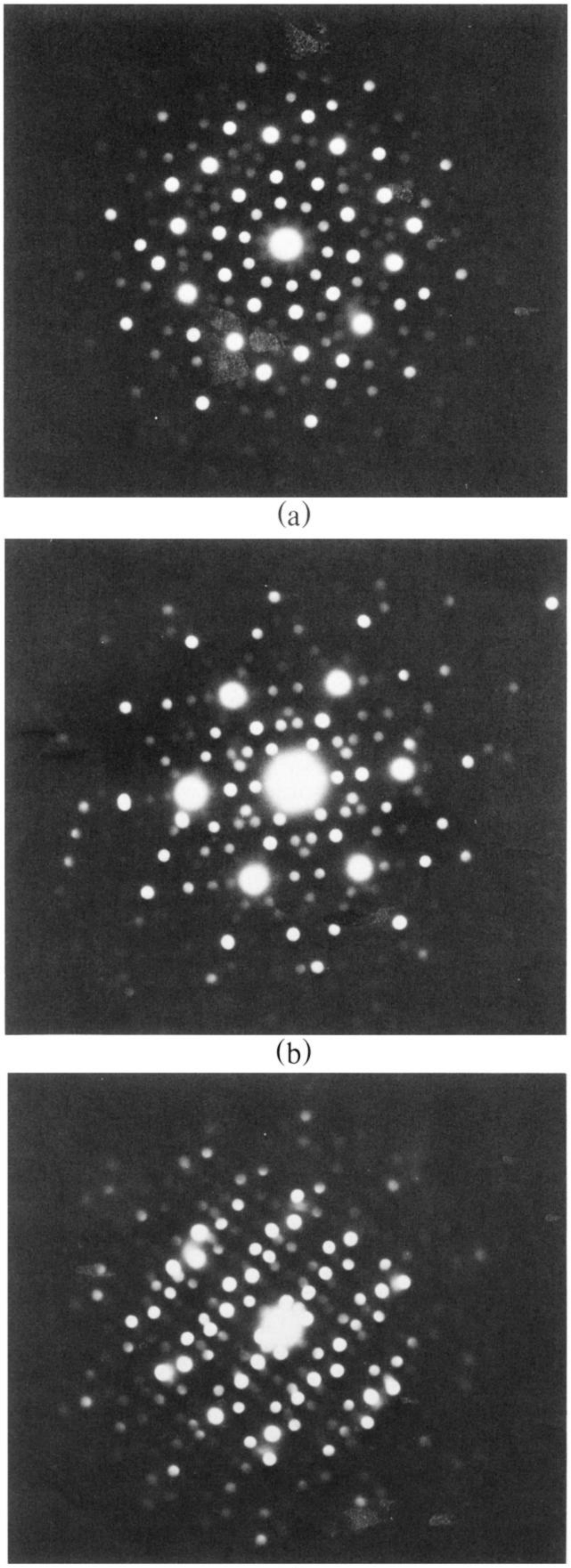
(a)

(b)

(c)

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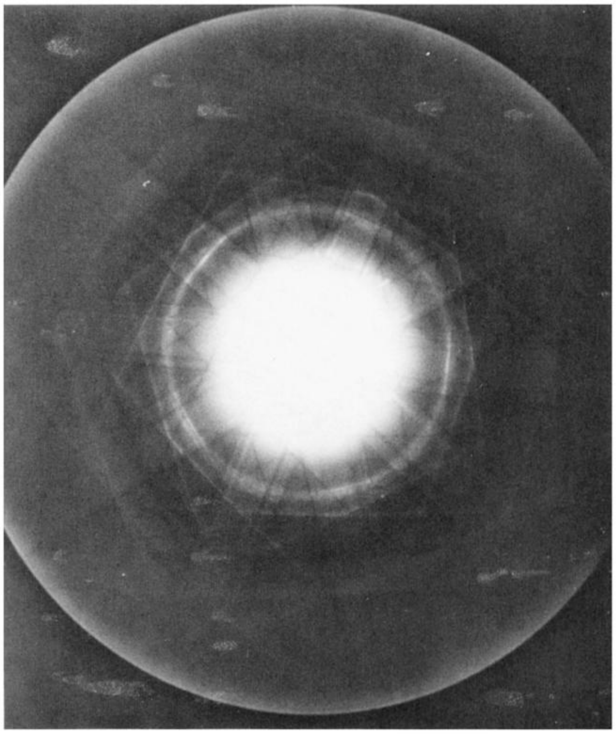

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