

X-ray diffraction from single Al_6CuLi_3 grains showing five-fold symmetry

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Abstract. We present here the detailed results of X-ray diffraction from single quasicrystals of Al_6CuLi_3 . X-ray precession photographs taken down the two-, three- and five-fold axes along with rotation and zero-level Weissenberg photographs are shown. Preliminary analysis of the diffraction data rules out the twin hypothesis.

Keywords. Quasicrystal; five-fold symmetry; X-ray diffraction.

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1. Introduction

Ever since the discovery by Shechtman *et al* (1984) of rapidly quenched $\text{Al}_{86}\text{Mn}_{14}$ alloys showing the five-fold rotational symmetry, tremendous progress has been made towards understanding these structures (Gratias and Michel 1986; Mackay 1987). However the atomic structures have not yet been elucidated fully. Several models have been proposed which describe the structure of these icosahedral alloys, otherwise known as quasicrystals: (a) the multiple twinning of cubic cells (Pauling 1987), (b) the icosahedral glass in which the icosahedral units are randomly packed in the same orientation (Stephens and Goldman 1986) and (c) three-dimensional Penrose tiling (Ogawa 1986). The evidences against the twin hypothesis are numerous, while no conclusive result has been published so far in favour of any of the other two models. In these circumstances, the possibility of better models cannot be ruled out.

Efforts that have been made to grow larger size quasicrystals in order to determine their structure by X-ray diffraction have been reasonably rewarding. Dubost *et al* (1986) and Bartges *et al* (1987) showed the formation of millimetre size quasicrystals in Al_6CuLi_3 by slow solidification. In this article we present the detailed and new results of X-ray diffraction from a single grain of Al_6CuLi_3 .

2. Sample preparation

The alloy of composition Al(65·3 wt%), Cu(27·5 wt%) and Li(7·2 wt%) was prepared from an Al-Cu master alloy and pure lithium. The alloy was later remelted and

directionally solidified with an imposed temperature gradient and withdrawal velocity (Rao and Sekhar 1987). The specimens for transmission electron microscopy (TEM) were prepared by electropolishing in a solution of 3:1 methanol:nitric acid at 13V DC and at -20°C (253 K). The TEM studies established the presence of large size grains of T2 phase. Figure 1 shows the selected area electron diffraction patterns taken from a single grain of Al_6CuLi_3 . Single quasicrystalline grains were extracted from the alloy by polishing and then by etching with nitric acid and cutting along the grain boundaries under an optical microscope. The specimens were typically $0.5\text{ mm} \times 0.5\text{ mm} \times 0.2\text{ mm}$ in dimensions and just sufficient for X-ray diffraction studies.

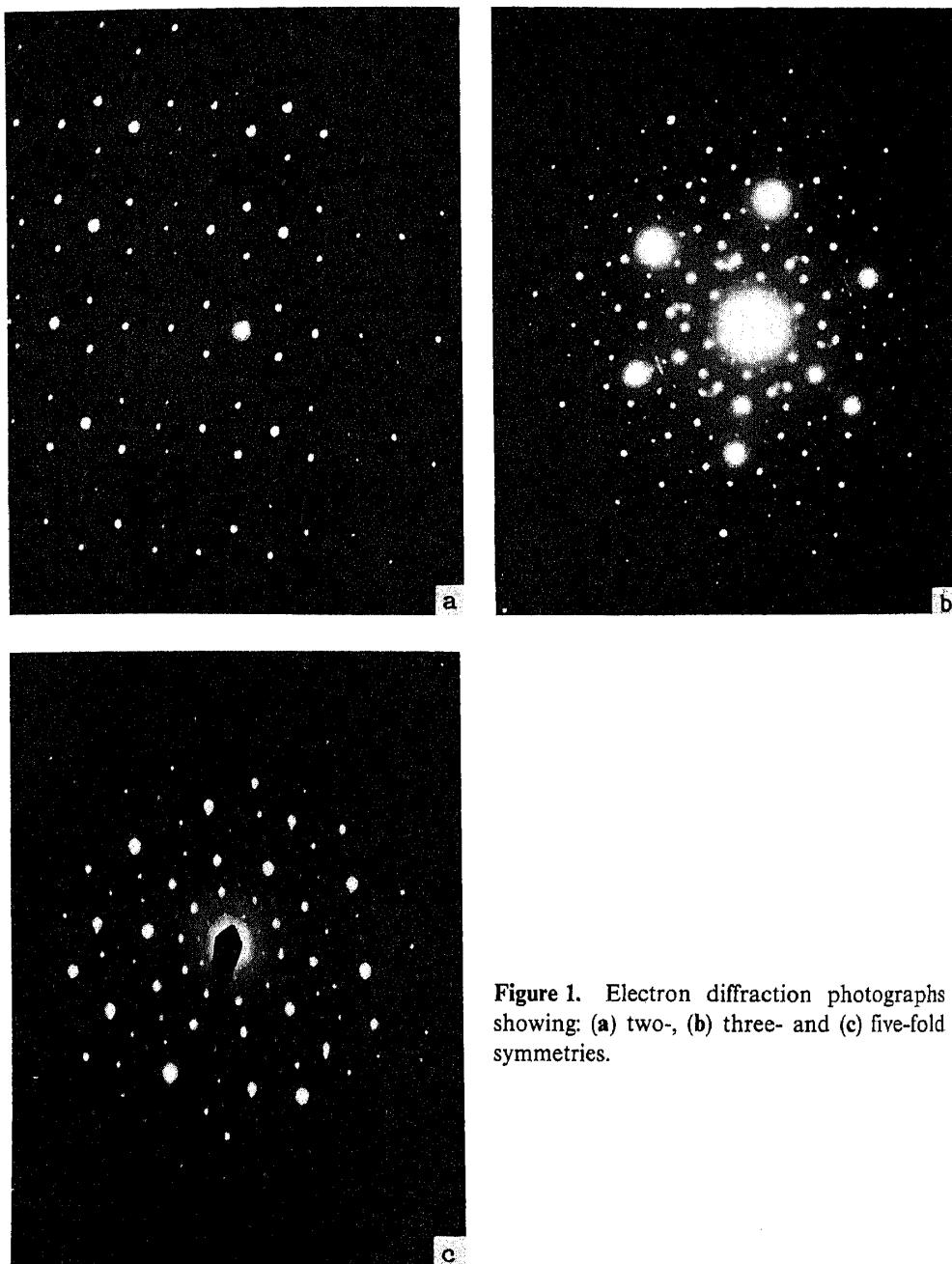


Figure 1. Electron diffraction photographs showing: (a) two-, (b) three- and (c) five-fold symmetries.

3. X-ray diffraction studies

One such sample was mounted on a precession camera. Several trial exposures at different orientations indicated the existence of two-, three- and five-fold symmetries. It was aligned such that one of the two-fold axes coincided with the spindle axis and another perpendicular two-fold axis with the X-ray beam. Figure 2a shows the zero level precession photograph down the two-fold axis with MoK_{α} radiation and $\bar{\mu} = 15^\circ$. Rotation by 90° about the spindle axis showed another two-fold axis, showing that there are three orthogonal two-fold axes. Figures 2b and c show the zero level photographs down the three- and five-fold axes after rotating about the spindle axis by 20.9° and 58.3° respectively. Similar three- and five-fold directions are marked in figure 2a which are at 20.9° and 58.3° from the vertical two-fold directions. Figures 2b and c show the evenfold symmetries 6 and 10. The actual symmetries could be either 6 and 10 or 3 and 5. To identify these symmetries unambiguously, higher layer photographs down these axes were recorded. The higher layer photographs in figure 3 confirm only the three- and five-fold symmetries. These two symmetry axes, in addition to a two fold axis, are perpendicular to another two-fold axis, which is against the conventional crystallography. The 532 symmetry and the various angles between the symmetry axes are compatible with the symmetry of the icosahedron.

The two axial lines in the zero plane of the two-fold axis are identical, but not related by a four-fold symmetry. In addition, the spacings of the layer lines are non-integral and they follow $1 - \tau$ relationships (table 1). So the reflections could not be assigned smaller Miller indices corresponding to a smaller unit cell. But it can be approximated to a larger unit cell, corresponding to which the reflections also take larger Miller indices.

The precession photographs contain only the low angle reflections. To check these observations for the high angle reflections, rotation and zero-level Weissenberg photographs were recorded about the same mounted axis with CuK_{α} radiation (figures 4a and b). The two-, three- and five-fold lines are marked in the Weissenberg photograph. The angles between them are the same as those observed in the precession photograph.

The layer lines are very closely spaced in the rotation photograph. Further spacings of the layers are non-integral, indicating that many intermediate layer lines are missing (table 2). If these missing layers are also taken into account, then it clearly indicates that the axial length along the rotation axis is very large.

Analysis of the two-fold pinacoidal lines of the Weissenberg photograph shows only very few reflections. These reflections have non-integral spacings and follow $1 - \tau$ relationship. The festoons drawn for the non-axial reflections intersect the axial lines, where there are no reflections. Further, many layers themselves are missing, suggesting that many reflections are absent on these axes too. This confirms that the axial lengths along these two fold axes are also large.

The possibility of large cell-dimensions is well established from the low angle reflections in the precession photograph on one hand and the low and high angle reflections in the rotation and Weissenberg photographs on the other hand. However, the number of reflections for such a large crystallographic unit cell is too small. This implies that very many reflections are absent. This is unusual for cell dimensions with only crystallographic symmetries. This argument leads to the conclusion that there are additional site symmetries which together with the crystallographic symmetries impose

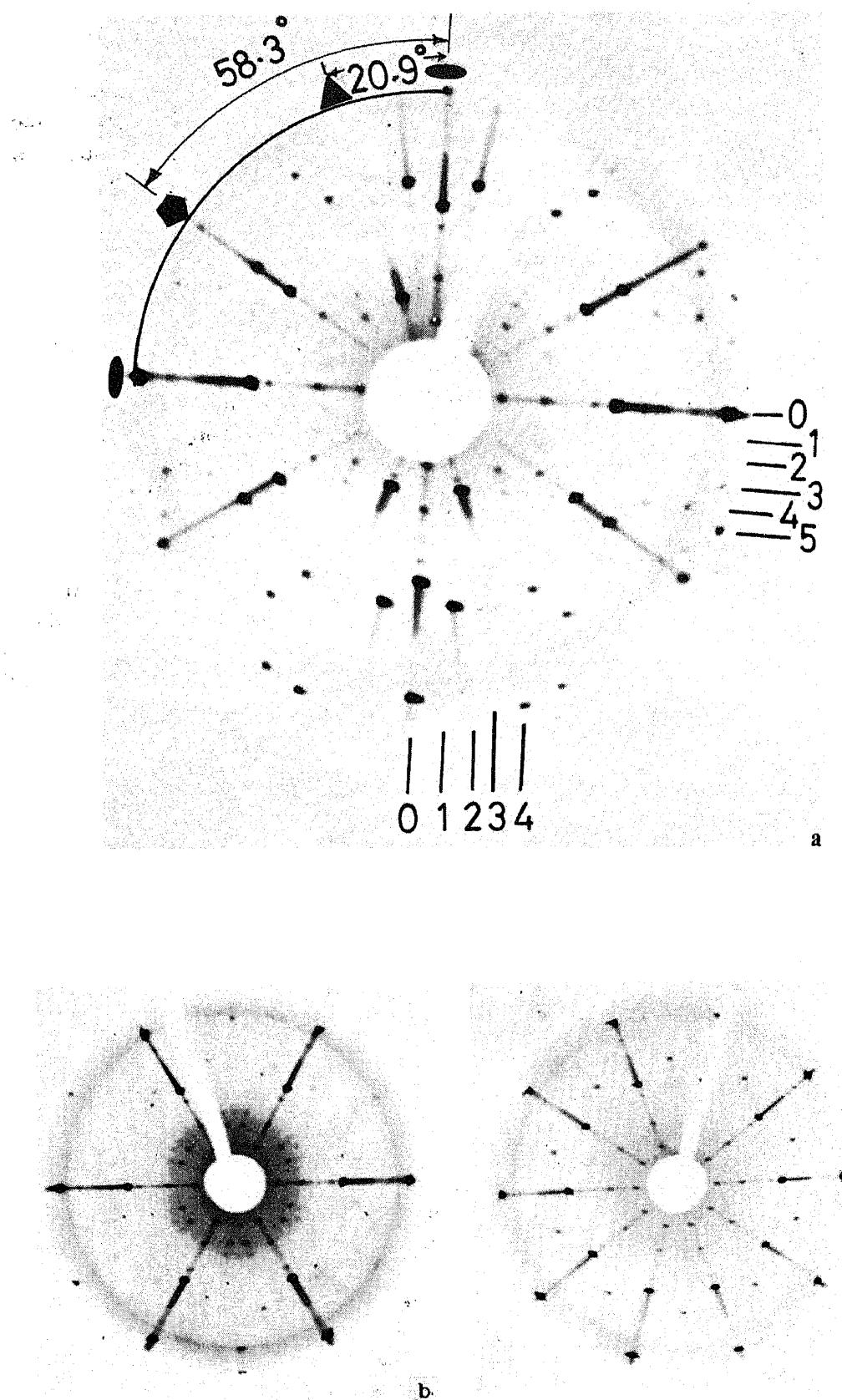


Figure 2. Zero-level precession photographs down: (a) two-, (b) three- and (c) five-fold axes (MoK_α , $\bar{\mu} = 15^\circ$).

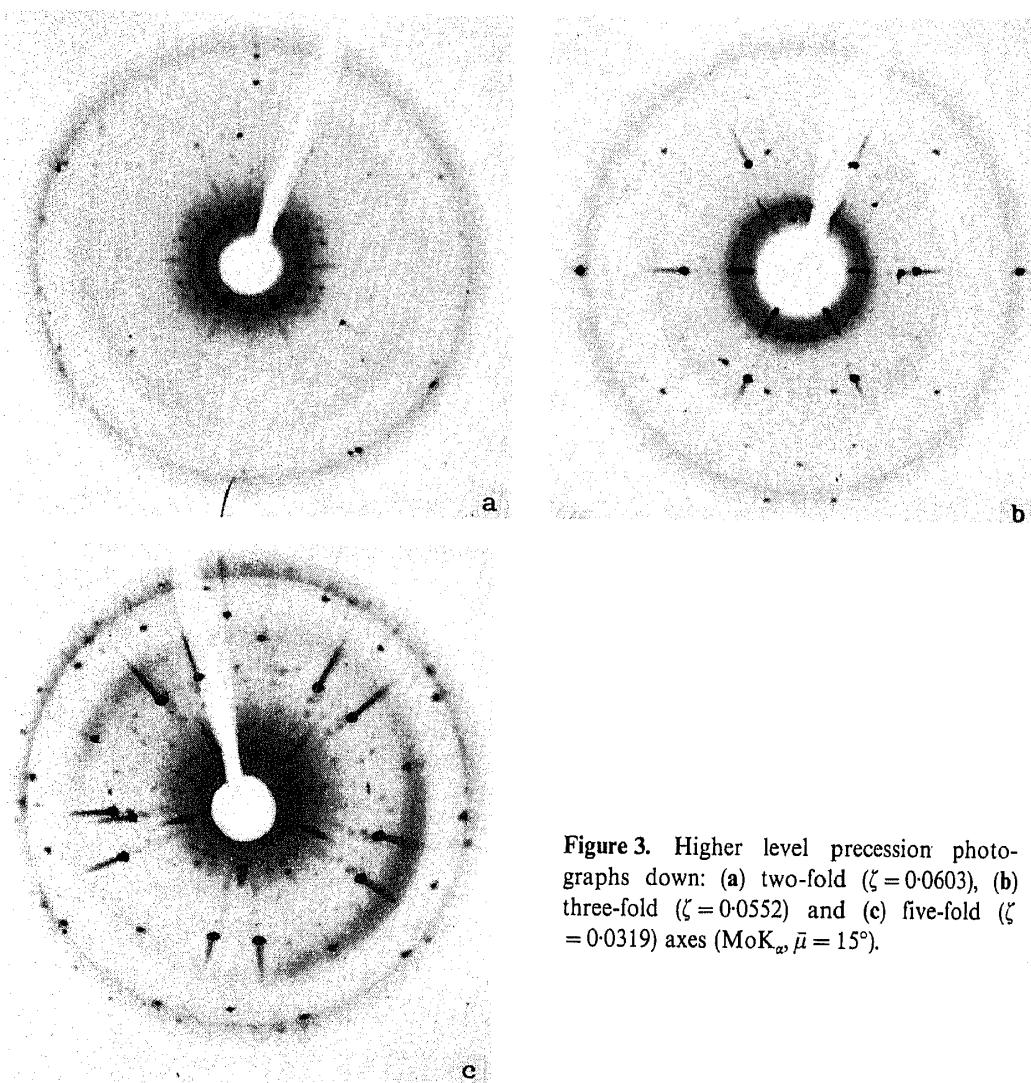


Figure 3. Higher level precession photographs down: (a) two-fold ($\zeta = 0.0603$), (b) three-fold ($\zeta = 0.0552$) and (c) five-fold ($\zeta = 0.0319$) axes (MoK_{α} , $\bar{\mu} = 15^\circ$).

Table 1. Spacings of a few layer lines in the zero-level precession photograph down the two-fold axis. Serial numbers correspond to those marked in figure 2a.

(a) horizontal		(b) vertical	
Sl. No.	Spacings (Å)	Sl. No.	Spacings (Å)
1	18.9275	1	12.0246
2	9.5040	2	5.9317
3	6.0174	3	5.3478
4	4.5847	4	3.6984
5	3.6907		

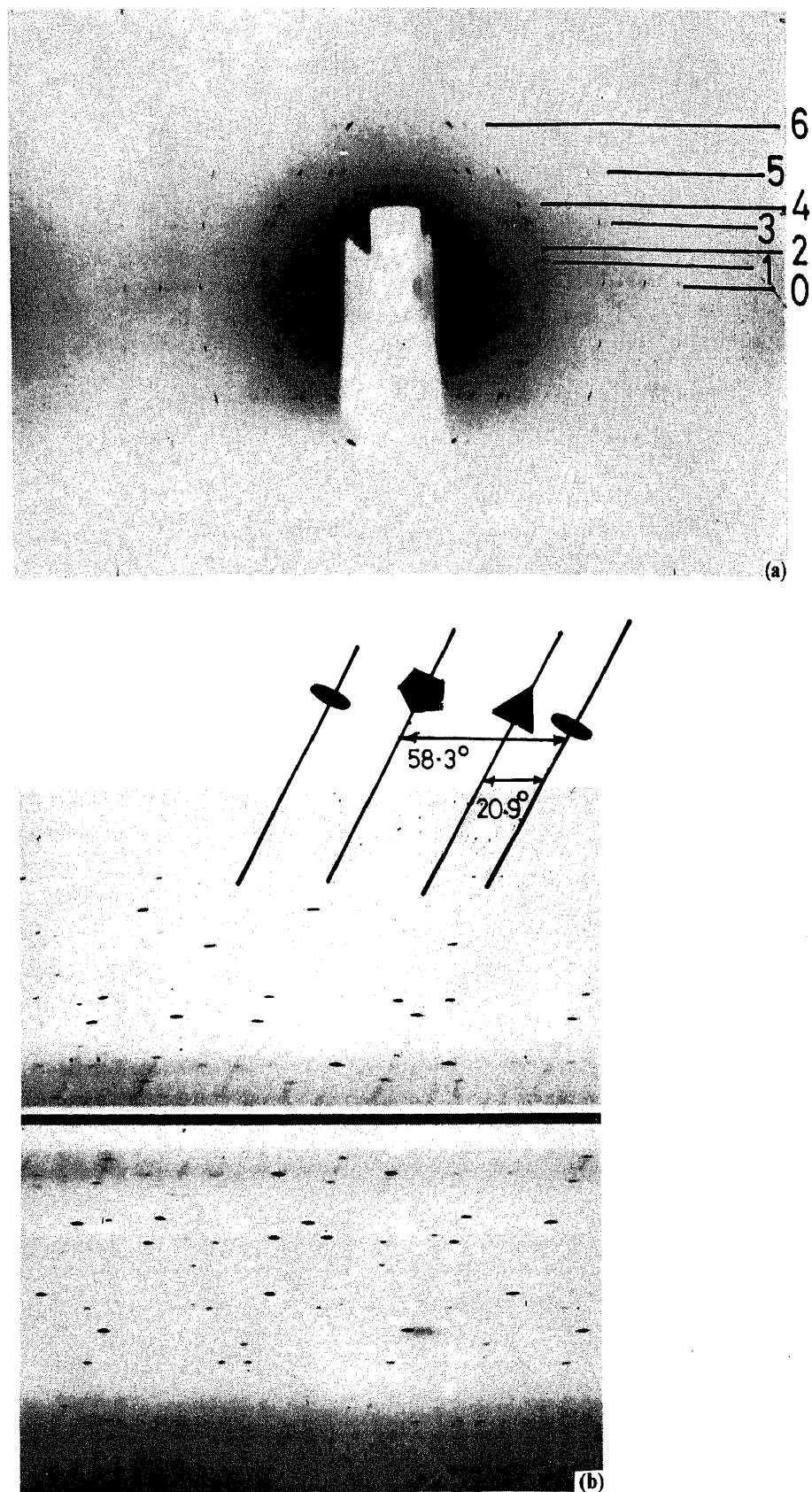


Figure 4. (a) Rotation photograph about the two-fold axis (CuK_α). (b) Zero-level Weissenberg photograph about the same axis (CuK_α).

Table 2. Spacings of a few layer lines in the rotation photograph. Serial numbers correspond to those marked in figure 4a.

Sl. No.	Spacings (Å)
1	12.0377
2	7.3749
3	4.5770
4	3.6903
5	2.8155
6	2.2741

new systematic absence conditions. These site symmetries may be the additional two-, three- and five-fold symmetries.

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