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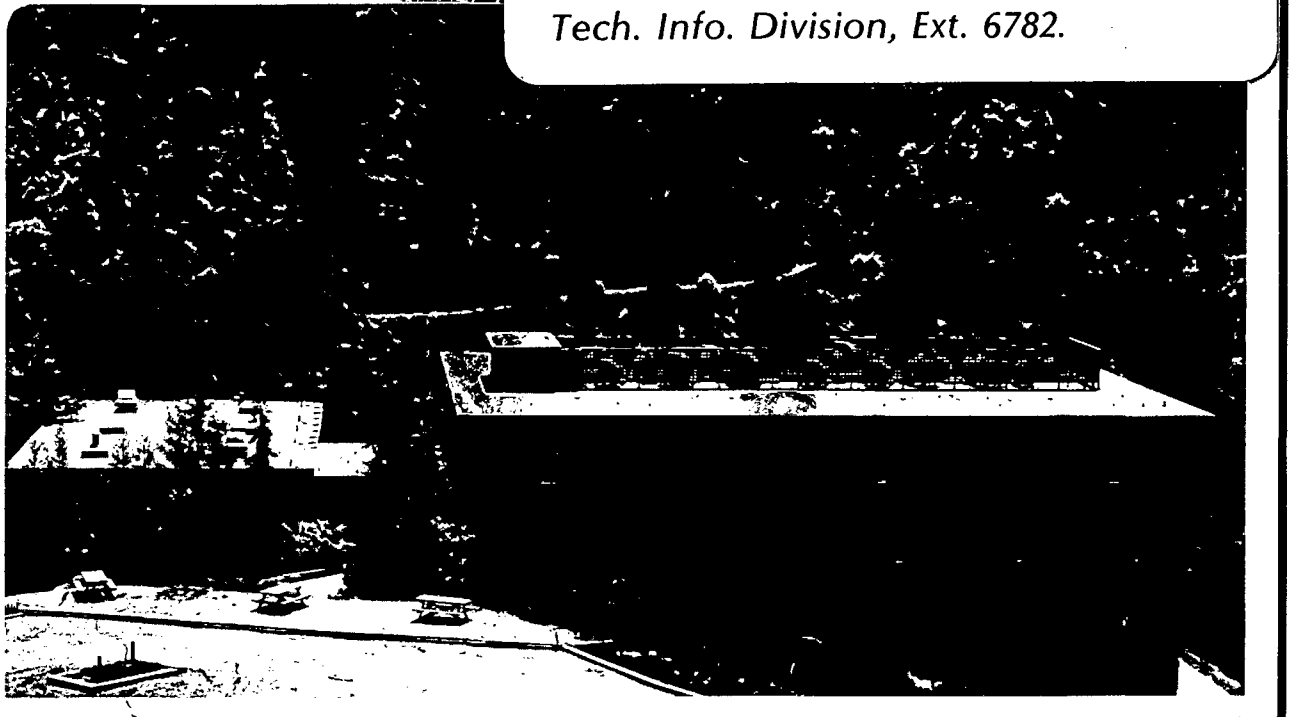

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INTRODUCTION Although the analysis of structure has been one of the primary objectives of electron microscopy for the past fifty years, it has been only relatively recently that the technique has demonstrated its potential for the complete (atomic level) determination of surface and interfacial structure. A number of technological achievements are responsible. For years, surfaces were studied exclusively with scanning systems and interfaces with transmission systems; this is no longer the case. Surfaces were constantly and drastically modified by the hostile "vacuum" environments of electron-optical columns; this is also no longer true. Finally the most interesting aspects of surface and interfacial structure, those local deviations in bulk crystalline order which represent defects, were frequently beyond the resolution limits set by probe size or lens aberrations and this is thankfully no longer a limitation as well. In fact, even since the last International Congress, applications of electron microscopy have brought the study of surface and interfacial structure much closer to the atomic level. The purpose of this review is to identify some of these recent developments, summarize their application to the microstructural analysis of surfaces and interfaces and indicate where they have made new contributions to the science of materials.

THEORETICAL MODELS The existing models of surfaces and interfaces with which the microscopist seeks contact are rather highly-developed atomistic representations of structure and they basically take one of two discrete formulations: (a) geometrical solutions which yield a crystallographic "best fit" or (b) energetic solutions where the local geometry is permitted to seek a low-energy configuration established by the minimization of some assumed potential distribution. Details of these theories are available in several comprehensive reviews [1-3], and are briefly highlighted below.

The atomic interpretation of surface phenomena relies heavily upon the Terrace-Ledge-Kink (TLK) model of surface structure (Fig. 1) which admits to the true dimensionality of a surface, i.e. that an exposed crystalline surface will consist of atomically flat terraces connected at different elevations by ledges (or steps) which themselves might be connected at different locations by kinks. Other commonly described surface defects are adsorbed atoms (adatoms) and vacancies, as shown in Fig. 1. All of these geometrical features of surface structure have been cited in explaining surface properties, e.g. transport phenomena, segregation, catalytic activity and crystal growth kinetics [2].

The description of a free surface as a simple termination of the bulk lattice has not always been favorable, however. For example, surfaces have been found to undergo relaxation processes [5] which might either be simple monolayer translations of fractional lattice coordinates ("normal" relaxation) or more complex ordering into new two-dimensional crystalline lattices ("reconstruction"), particularly in the presence of an adsorbate. Successful modeling of these structures has been considerably more difficult [6], although recent computations using a self-consistent pseudopotential method [7] have been reported, wherein the electronic structure of the free surface is also deduced.

The verification of these models of surface structure has for the most part been based upon LEED studies [2]. Complete surface structural determination, however, awaits the detection of the morphologies of surface relaxation events which completely elude detection by LEED; this of course requires imaging and therein lies the challenge for the microscopist.

In a similar manner, the atomic interpretation of interfacial phenomena relies heavily upon the various transition lattice models [1] of interfacial structure, of which the coincidence site lattice (CSL) and more general O-lattice are the most popular. Based upon the assumption that an interface will have lowest energy if its bordering crystals have best fit, the interface is described as a crystallographic plane of a type of superlattice of both misoriented crystals which is continuous across their boundary (Fig. 2). The most notable successes of these models has been in the predictions of "special" boundaries which have distinctive properties [8]. In homophase boundaries at least, these models are fundamental to the description of atomic order within an interfacial plane, and as the starting point for the energy minimization schemes used to compute relaxed boundary structures [9]. Complications arise when applied to heterophase boundaries, although these are not intractable, and a number of promising approaches have emerged [10,11].

Of course, the most obvious features of interfacial structure are not the regions of good fit but the regions of poor fit, particularly the core regions of interfacial dislocations. In fact, a salient objective of all models of interfacial structure is the prediction of the DSC translations associated with these interfacial dislocations (see Fig. 2), which in turn requires carefully contrived experiments in electron microscopy. Even more care (and resolution) is needed to detect the ordered polyhedral units predicted to occur as a fundamental structural entity in all mechanically stable interfaces. [12].

EXPERIMENTAL METHODS It follows from the above discussion of modern theoretical models that any scientifically meaningful probe of surface or interfacial

structure must in general be done at near-atomic resolution. The special circumstances under which such performance levels can be achieved are now described.

FIM The first method with promise of atomic resolution of surfaces and interfaces was field ion microscopy and its operating principles and applications to grain boundaries have already been reviewed [13]. In fact, the FIM and its accessorized offspring, the imaging atom probe (IAP), are only capable in certain circumstances [14] of providing images which indicate contiguous atom positions (see Fig. 3).

The most recent developments in FIM and IAP instrumentation have been chiefly in automation of data acquisition and analysis, and these have been used to monitor surface atom diffusion and clustering, nanometer-scale composition profiles and fractional-nanometer grain boundary topology, all reported [15] in the 1981 EMSA Presidential Symposium on the topic. Unfortunately, the FIM and IAP are not produced commercially, accounting in part for their low popularity. Nevertheless, their potential in the study of surfaces and interfaces, particularly when coupled with electron optical instrumentation, has been amply demonstrated and supported by the resurgence of interest in these techniques.

STEM Among the scanning electron optical devices, the dedicated scanning transmission electron microscopy (STEM) with field-emission gun provides the highest resolution capabilities for surface and interfacial structural analysis [16], and it does so in a number of operating modes. The more recent imaging innovations exploit the fact that the STEM small-aperture axial detector can be placed after an energy loss spectrometer to select scattered electrons which have suffered

discrete loss events. Of itself, this feature forms the basis of "low loss imaging" methods which are well-known in SEM [17], or when displayed as a difference image with the annular aperture dark field signal, it yields the "z-contrast" method developed by Crewe et al. [18] for imaging heavy atoms on near-noiseless support films. These methods of imaging have been applied in the study of catalyst particles [19] for the limited range of appropriate specimens which are available. However, their application to atomic level structural analysis has not yet surfaced.

An alternative imaging mode [20] makes use of surface Bragg scattered electrons to obtain reflection images with enhanced depth of field and a lateral resolution (normal to the distortions along the beam direction) of ~ 10Å. Under these conditions, surfaces ledges of a few unit cells in height are imaged quite clearly (Fig. 4).

Ultimately the most successful mode of operation in STEM for atomic level structural information remains the microdiffraction mode. This has been demonstrated by the elegant experiments of Cowley [21] wherein the incident probe is directed along a flat parallel face of an MgO crystal and moved incrementally from the vacuum into the crystal while microdiffraction patterns are being recorded. The results demonstrate markedly detectable variations in the scattering distribution which can in principle be interpreted in terms of the three-dimensional atomic structure of the surface.

TEM The superior resolution capabilities of the transmission electron microscope (TEM) for imaging of atomic structures are well-known; yet its application to the study of surfaces began slowly in 1974 [22]. This early method was based upon

amplitude contrast imaging in dark field using one of the forbidden "surface lattice" reflections from a Au film. The more recent variations of this approach have been in bright field where monolayer ledges were observed on graphite [23] and MgO [24] crystals.

Using a phase contrast imaging method, Krakow [25,26] extended the early work on Au films to show directly the morphologies and distribution of 2.48Å surface lattice periodicities, where the interpretation of results was based upon computer simulations involving saturation sampling (65,536 points) of the reciprocal space scattering distribution.

Nonetheless, the most exciting development in the area of surface imaging has been one of hardware: the ultra-high vacuum (UHV) modification of a TEM to permit meaningful operation in a reflection imaging mode by preventing the intrusion of surface contamination effects [27]. An example is shown in Fig. 5, taken from the work of Yagi [28]. The micrograph is a clean (111) Si surface where the wavy lines are atomic ledges of unit height and the straight horizontal line at the center of the figure is a screw dislocation at the termination of one of the surface steps. Additional applications of this method to studies of surface topography, surface reconstruction, condensation (adsorption) and surface nucleation have been summarized by Takayanagi [29].

In the study of interfacial structure, the TEM has persistently maintained its advantage, particularly with reference to the atomic models of internal boundaries [30,32]. Current efforts continue to be directed toward the direct imaging of

atomic structure [13], where to date, the larger unit cell, tetrahedrally coordinated semiconductors have been more amenable to analysis [33,35].

A recent result [36] on a smaller-unit-cell bcc material is shown in Fig. 6. The image shows all atom positions across a $\Sigma 41$ asymmetrical tilt boundary in Mo as recorded in a JEM 200CX equipped with ultrahigh resolution goniometer. Direct contact with the O-lattice construction for this boundary is obtained at a level of resolution which enables the DSC component along the beam direction to also be accurately deduced; confirmation of the displacements is of course achieved by complementary diffraction analysis [36].

SUMMARY The scope of this review is intentionally limited to those research efforts which directly address the most current theoretical models of structure used to explain the properties of materials; hence the emphasis on atomic resolution. Yet with this approach there is some danger of missing the forest for the trees. It has been pointed out [14], for example, that the most serious limitation of the atom probe is its inability to scan microstructures at low magnification! Obviously the examination of surface and interfacial structure should involve a combination of methods, including chemical analyses (where, of course, the STEM would exhibit its true versatility). Indeed, the developments in all of these areas is highly encouraging.

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Fig. 1. Schematic representation of the Terrace-Ledge-Kink (TLK) model of surface structure (after Gjostein, ref. 4).

Fig. 2. Transition lattice construction for two cubic lattices rotated by 36.9° about a common [001] axis. One in five base lattice points are in coincidence. Note that every other O-lattice point is a point in the CSL lattice.

Fig. 3. Computer simulation of an FIM image for a [001] oriented f.c.c. crystal. From emitter tip geometry alone, adjacent atom images can only be achieved in the high-index pole regions of the specimen (ref. 13).

Fig. 4. STEM reflection image of surface steps on an MgO crystal (courtesy J. M. Cowley, ref. 21).

Fig. 5. Reflection image of (111) Si surface showing terrace-ledge-kink structure, described in text (courtesy of K. Yagi, ref. 28).

Fig. 6. High resolution TEM image of a Σ 41 boundary in Mo showing all atom positions at ~ 2.3Å level. Burgers vectors of core dislocations are indicated.

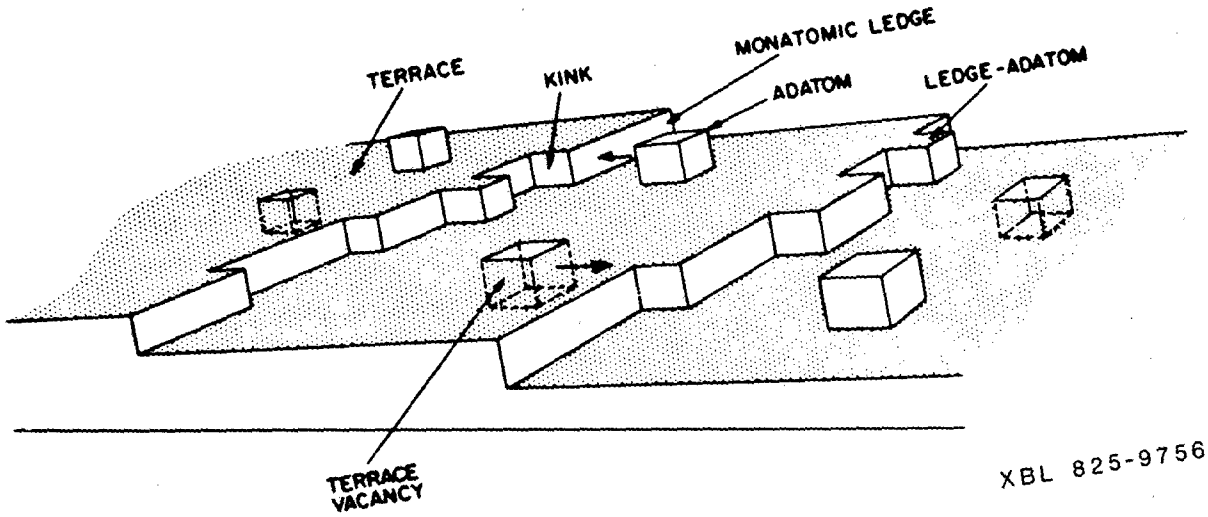
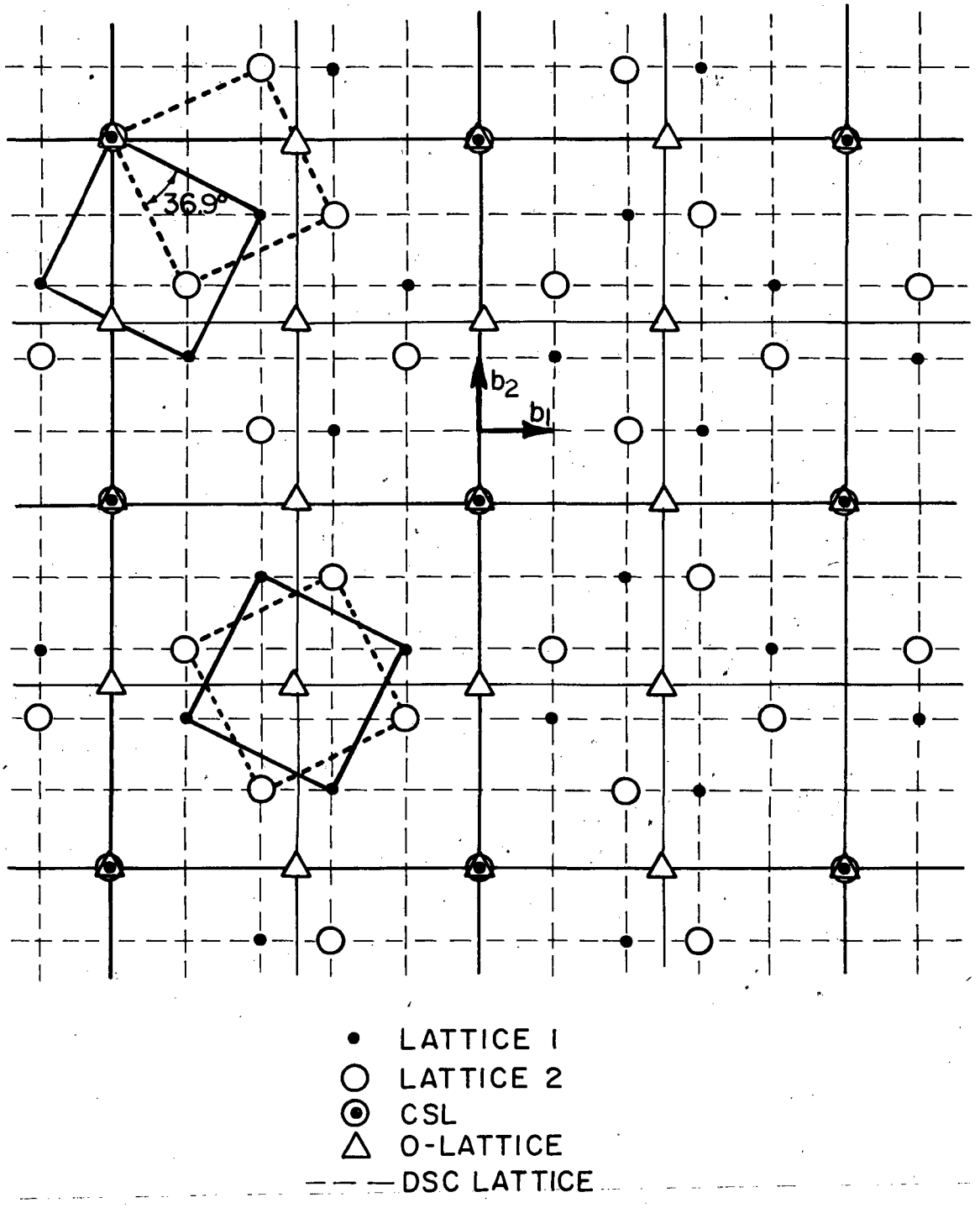

TERRACE
KINK
MONATOMIC LEDGE
ADATOM
LEDGE-ADATOM
TERRACE VACANCY
XBL 825-9756

Fig. 1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36.9°
b2
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CSL
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Fig. 2

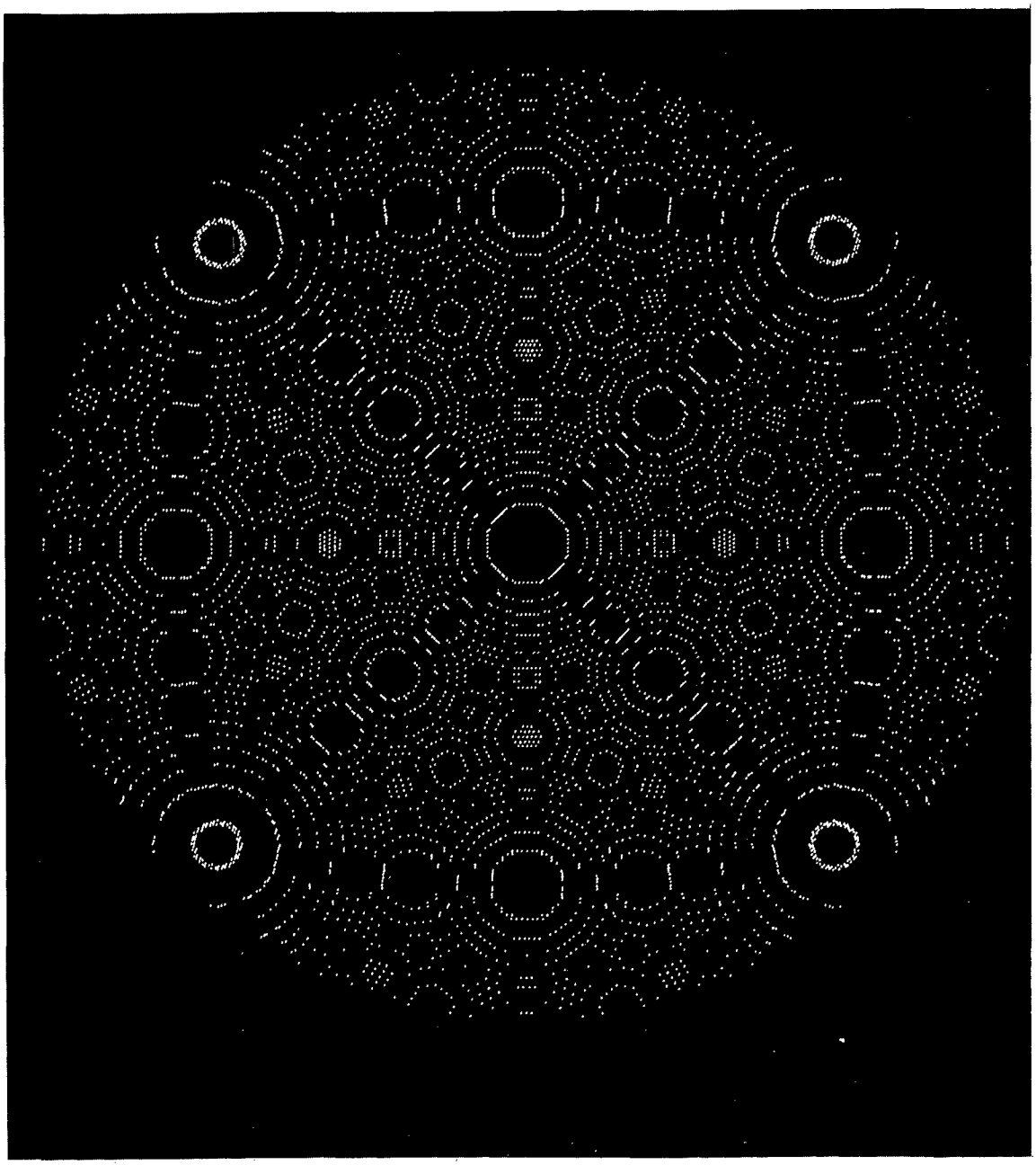

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Fig. 3

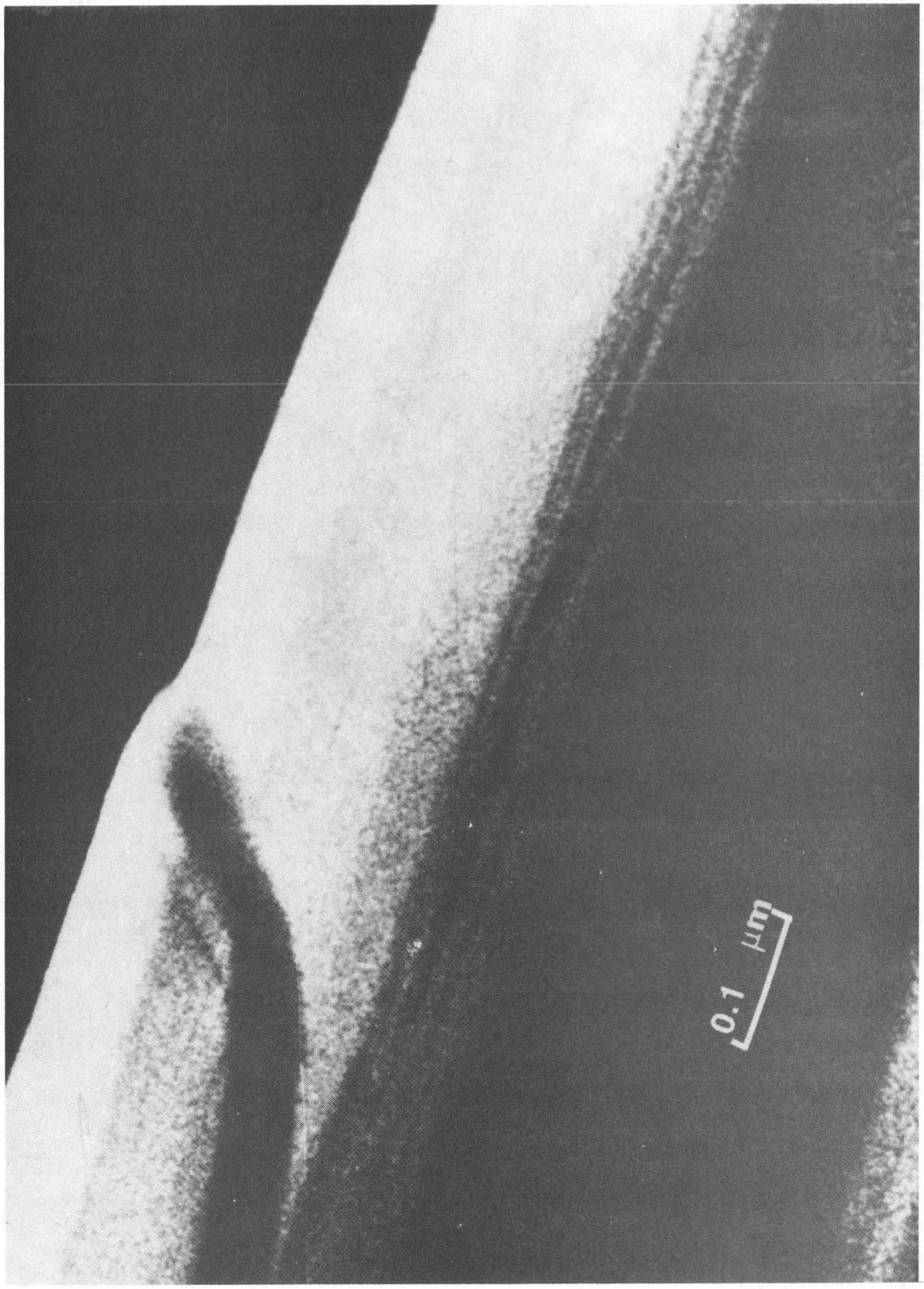

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Fig. 4

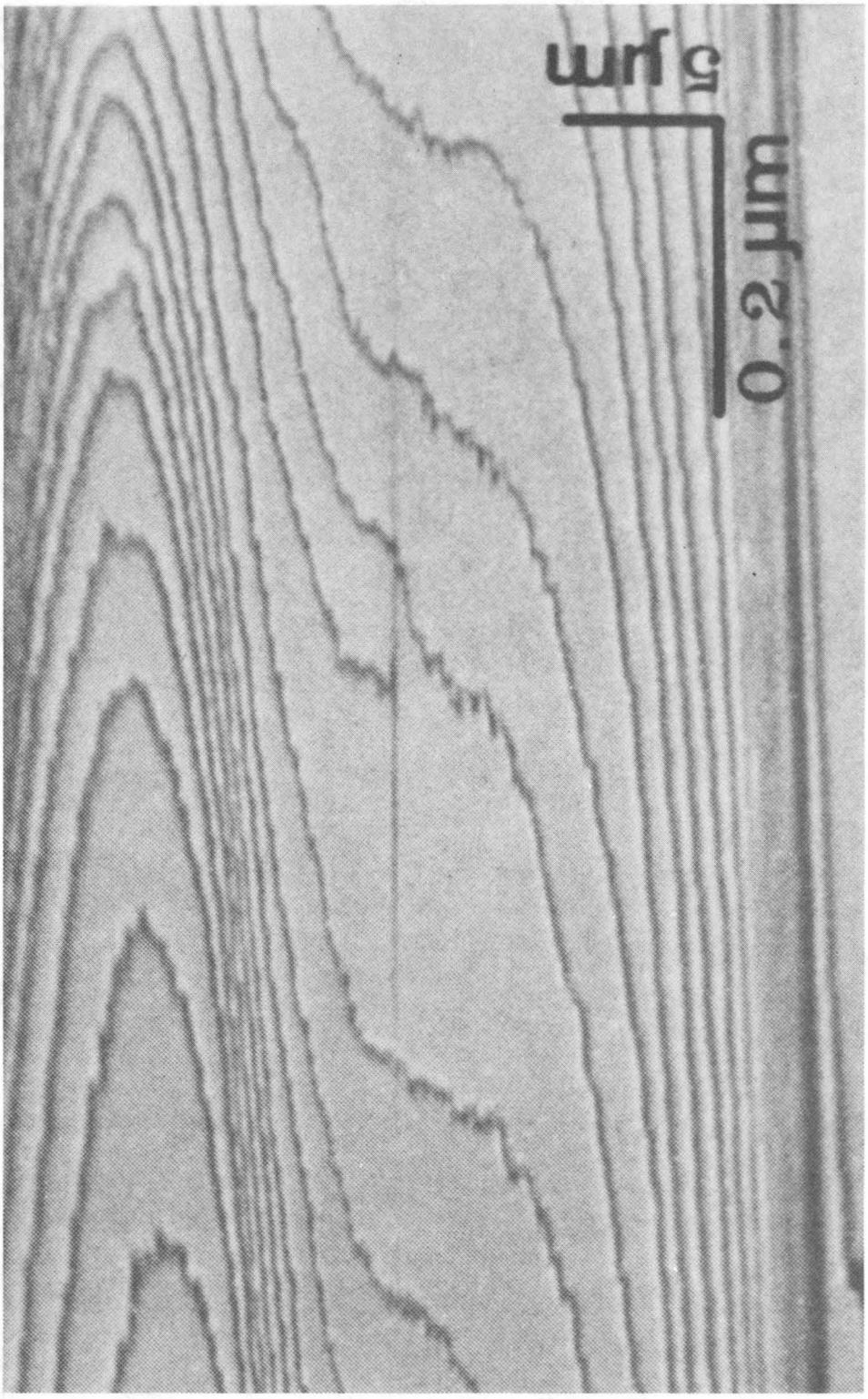

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Fig. 5

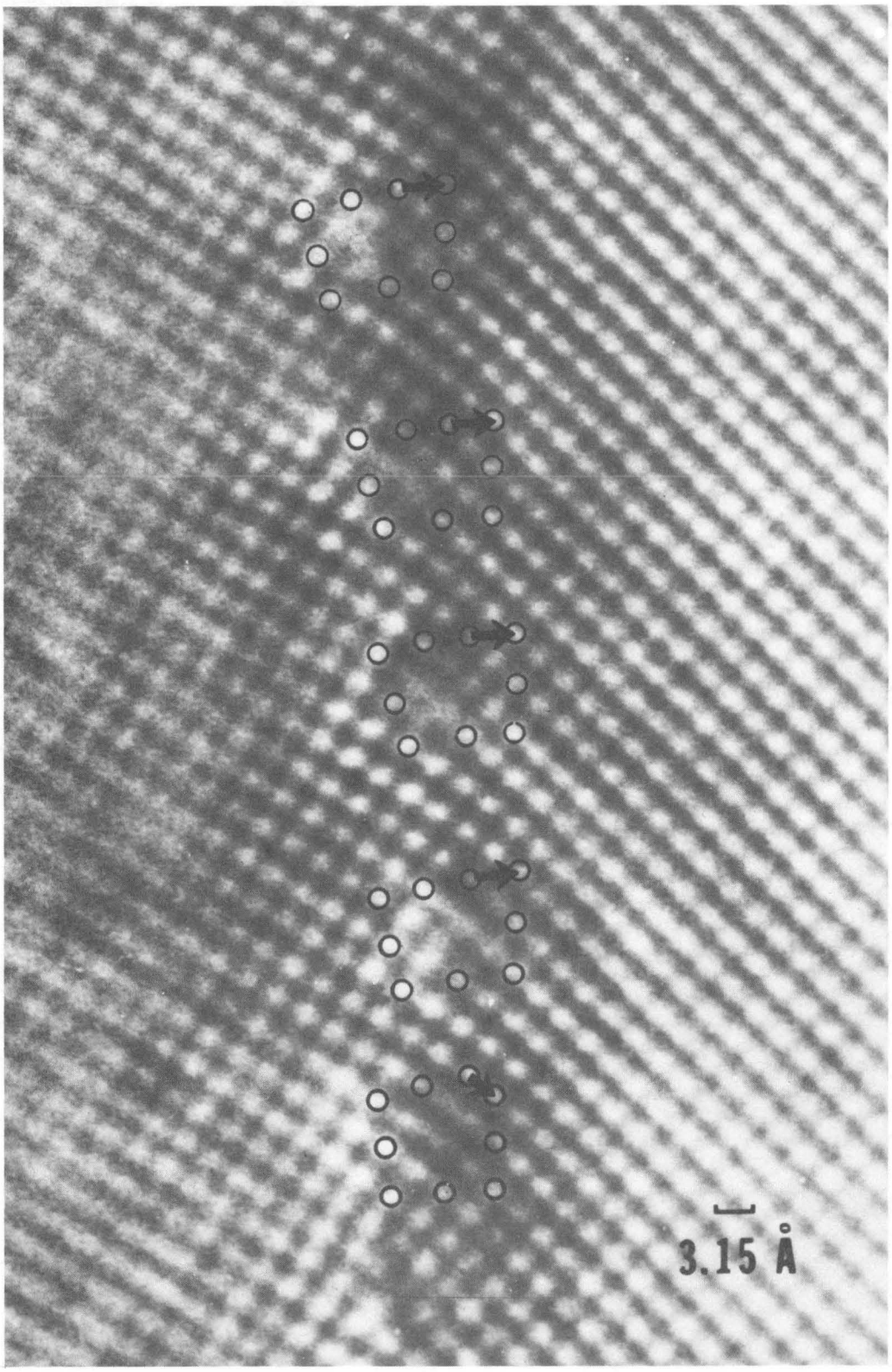

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Fig. 6

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