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High Resolution Electron Microscopy Studies of the Early Stages of Decomposition in Alloys and Ceramics

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1. INTRODUCTION

The technique of high resolution electron microscopy has reached widespread acceptance as a materials characterization tool, chiefly due to the availability of new research instruments which have increased resolution as well as enhanced operator convenience. At its best, the method provides direct images of the atomic structure of solids. However, the attainment and interpretation of such images remain widely differing events and care is still required to avoid misrepresenting the true specimen structure by a random high resolution phase contrast image [1].

A phase contrast image is formed by the recombination of more than one beam which has been scattered by the specimen. The various scattered beams have different phases by virtue of their different path lengths along the optical system, and under the action of an objective lens, this produces image contrast. An image formed by phase contrast has the highest resolution because it is sensitive to the individual scattering centers in the specimen; nevertheless the resolution which is achieved depends upon the number of beams included in the imaging aperture as well as focus [1] (Fig. 1). Obviously, with knowledge of all specimen and instrumental parameters, image interpretation is greatly facilitated. Confidence in image interpretation can in fact be best supported by the computer simulation of high resolution micrographs [2], and rapid computational methods [3] have made even real time simulations possible.

In this paper, some applications of high resolution electron microscopy to studies of the early stages of decomposition in alloys and ceramics is described. Two important parameters of the decomposition process, structural evolution and compositional variation, are specifically addressed. Since these applications push

the limits of both image formation and computer simulation, a number of critical technique-related problems are identified.

2. SPINODAL DECOMPOSITION

The first of these problems concerns the use of the lattice imaging technique for monitoring the composition modulation resulting from spinodal decomposition [4]. In this case the phase scrambling induced by a slowly varying lattice parameter within the specimen can produce widely varying contrast effects, requiring detailed knowledge of the variation of the lens transfer function across the distribution of elastic diffuse scattering (satellites) in reciprocal space [5,6]. Once the transfer function is understood, however, the interpretation of such images becomes straightforward. It is emphasized that the high spatial resolution afforded by phase contrast imaging is uniquely beneficial in this case because of the irregular pattern of decomposition in most alloys at the atomic level (e.g. Fig. 6, Ref. 4). The image simulations have assumed regular periodicities, accounting in part for the discrepancies which they suggest. Furthermore, the application of complementary spectroscopic and microdiffraction techniques has shown variations in composition which agree with those estimated from lattice images [7], in which composition has been related to fringe spacing [8,9].

3. INITIAL STAGES OF PRECIPITATION

Historically, an incipient precipitate was only classified as a new phase when it produced diffraction effects that were clearly distinct from its host matrix reflections. By this scheme, G.P. zones have been considered a pre-precipitation event since their presence merely modifies the diffracted intensity distribution around matrix reflections. Yet a recent application of high resolution electron microscopy clearly shows the advantages of the technique for spatial discrimination of discrete atomic clusters [10].

Figure 2 shows (a) the atomic model of a Ag-rich zone in an Al matrix according to Gragg and Cohen [11] and Fig. 2b shows the high resolution image of such a zone formed in an Al-4.2at%Ag alloy. The image agrees in every way with the model of an octahedral zone which has no internal ordering and points to the dominant crystallographic influence of the matrix phase exerted at the earliest stages of clustering. More importantly, it shows that the technique is extremely sensitive to the presence of such clusters, even when the diffraction data is, at best, diffuse.

4. PERIODIC STRUCTURES

In addition to the case of modulated spinodals as discussed above, atomic resolution imaging is of great advantage in analysing more complex periodic structures, e.g. polytypes, polytypoids (structure changes due to composition fluctuations) ordered alloy/compounds, etc. which can be commensurate or non-commensurate. With the proper orientation of sample and imaging conditions, it is possible to read off the structure directly from the image, and in highly localized areas, without having to perform Fourier transforms on the diffraction pattern. The method is particularly useful when structures (and/or composition) vary over small volumes resulting in diffuse electron scattering, or when the sample is subject to irradiation damage, especially in a focussed beam. Examples have been given recently for polytypoids in AlN-SiO_2 ceramics in which three new polytypoids 33R, 24H and 39R were discovered [12], not previously identified by x-ray analysis. Other examples have been made for metallic compounds indicating modulations of wave rather than antiphase character [13]. Very recently an incommensurate modulated structure has been resolved in the ZrO_2-ZrN system (2.5 to 75 mol%ZrN) (Fig. 3) and although the oxygen and nitrogen ions have not as yet been resolved, it is likely that the modulation is due to pseudoperiodic fluctuations of nitrogen with respect to oxygen in layers corresponding to mixtures of Zr_7O_{14} and $Zr_7O_{11}N_2$ and the incommensurability

is due to deviations in spacing and/or orientation of the layers [14]. Clearly the availability now of electron microscopes with resolutions interpretable at 1.6Å means it may be possible to directly resolve the atomic composition in these layers [15].

Of course the interpretation of atomic level imaging requires painstaking efforts in specimen preparation (needing very thin ~100Å, clean specimens), microscope operation and performance--including taking images of the same volume in different crystallographic projections--hence the need for high angle tilting stages maintaining atomic resolution [15] and appropriate theoretical calculations for these projections taking into account all parameters [2]. A further advantage of high resolution at high voltages is that irradiation damage causing ionisation and other structural damage decreases with increasing energy due to the reduction of inelastic scattering cross-sections. The limit of course is that energy at the threshold for displacement (knock-on damage). This is why it is important to have a variable voltage atomic resolution microscope [15].

5. SHORT RANGE ORDER AND THE INITIAL STAGES OF ORDERING IN ALLOYS

The short range order (SRO) state in alloys is defined as a pre-ordering state existing exclusively above the ordering temperature. In-situ observations of the SRO state by electron microscopy and electron diffraction have only been partly successful due to limited instrumental resolution at high temperature, uncertainty about local crystal temperature, and surface contamination resulting from poor vacuum. Moreover, in situ experiments in thin foils are not always representative of bulk material. In order to overcome these problems and to be able to obtain information from high resolution microscopy, studies must be restricted to the quenched-in state. During the quench, however, the "ordering

spinodal" may be crossed, leading to an amplification of the associated concentration wave [16] or a state of long range order may establish itself already. For some alloys, however, the quenched-in state seems to reflect the true SRO state [17,18].

Of particular interest are those systems where the long range order (LRO) reflections and the SRO intensity maxima do not coincide, allowing a more detailed study of the evolution of LRO from the SRO state. In this respect, two different families seem to qualify:

(a) the Ni_4Mo-type systems featuring SRO intensity at <1 1/2 0> special points but LRO intensity at n/5<420> positions [19].

(b) the long period superstructures (such as CuAu, Cu_3Au or Cu_3Pd) featuring diffuse intensity around <100> and <110> positions.

An example from (b) illustrating the initial stages of ordering in $Cu_{70}Pd_{30}$ follows [20].

A [001] electron diffraction pattern of as-quenched $Cu_{70}Pd_{30}$ is shown in Fig. 4a. Apart from the intense basic fcc reflections, weaker ordering reflections are present around <100> and <110>. Such diffraction patterns have been intensively studied by Ohshima et al. [20,21] and it was emphasized that order parameters beyond the 15th neighbour play an important role in characterising the SRO diffuse scattering [21]. To image possible microdomains associated with the ordering or to gain information about the internal structure of such microdomains, three different imaging modes can be used depending upon the size of the objective diaphragm. As indicated in Fig. 4a, these are:

(i) a dark field image selecting all four SRO reflections around <110> to show randomly dispersed small ordered domains (Fig. 4b); (ii) a bright field high resolution image using a limited size aperture which excludes the basic fcc reflections (B in Fig. 4a) and clearly reveals the internal structure of the microdomains (Fig. 4c); (White dots two-dimensionally aligned along the cube directions and separated by 0.37nm match perfectly with the expected Pd ordering in an $L1_2$ type structure.) and (iii) a usual high resolution image using a very large aperture (C in Fig. 4a) which includes ordering as well as fcc reflections up to 200_{fcc} and reveals the maximum detail only limited by the instrumental resolution (Fig. 5).

Note in Fig. 4c that the cubic arrangement of white dots separated by 0.37nm matches perfectly with the expected L1 ordered structure for Pd atoms. Also in Fig. 5 the larger aperture gives extra information about the fundamental lattice only and obscures the ordered structure. This example illustrates that the most adequate resolution depends upon the problem and it is not straightforward that higher resolution will provide more information.

Using optical diffraction from the HREM negatives as a micro-diffraction technique, e.g. [4], "single crystal" diffraction patterns can be produced from such microdomains (Fig. 5c). It confirms that the internal structure of the domains is of the $L1_2$ type, giving rise in diffraction to a single spot at <100> and <110> positions. The four-fold splitting around <110> and the two-fold splitting around <100> (Fig. 2b) is introduced by the correlation between neighbouring domains as suggested by Hashimoto [22]. Similar results confirming the present findings are obtained for CuAu and Cu_2Au [23].

SUMMARY

Very high resolution electron microscopy can provide direct information on

the earliest stages of solid state transformations down to the atomic level provided that instruments are available with appropriate resolution and tilting capabilities and that interpretation is aided by computational analysis. This requires detailed information on all specimen and microscope operating parameters.

ACKNOWLEDGEMENTS

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Figure Captions

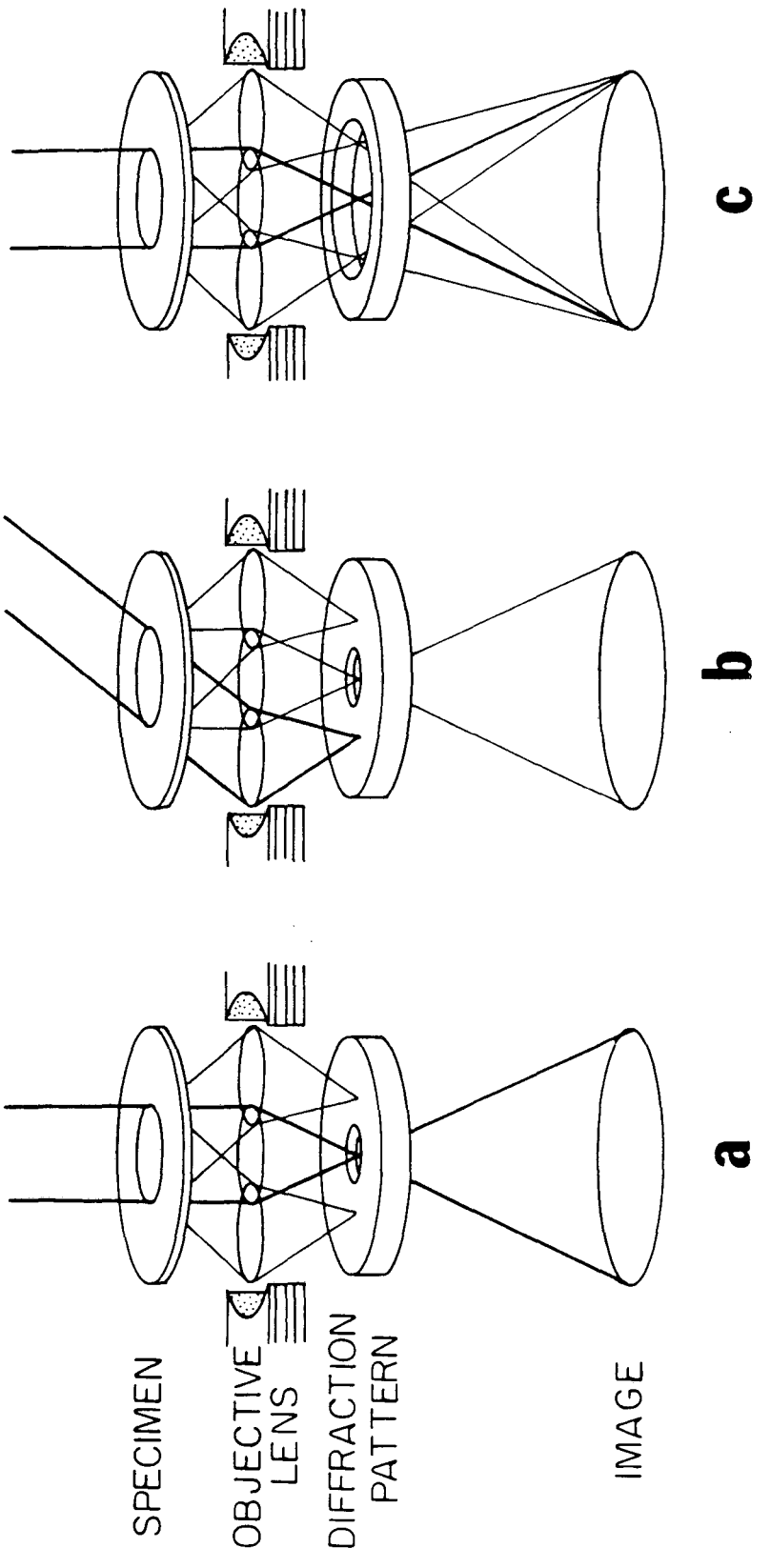
Fig. 1. Optical reconstruction showing image detail as a function of objective aperture size a) bright field imaging; b) dark field imaging; c) lattice-phase contrast imaging.

Fig. 2. a) Structural model and b) high resolution image of a G.P. zone in an Al-Ag alloy.

Fig. 3. a) High resolution image of [$\bar{3}21$] oriented ZrO_2-ZrN sample showing the transition from a regular superstructure to the incommensurate modulated structure. b),c) are laser optical microdiffraction patterns from the areas shown--the periodicity of the modulated area (c) contains commensurate and incommensurate superstructure reflections (Courtesy Acta Met., Ref. 14).

Fig. 4. a) [001] electron diffraction pattern of $Cu_{70}Pd_{30}$. Three different objective apertures used to obtain the images in Figs. 4b, c, and 5a are indicated; b) dark field image using aperture A indicated in Fig. 4a; c) bright field HREM image using aperture B in Fig. 4a.

Fig. 5. a) High resolution image using aperture C in Fig. 4a; b) optical diffraction from a larger area indicated B in Fig. 5a; c) optical diffraction of a single microdomain, indicated A in Fig. 5a.



XBL 807-5497

Fig. 1

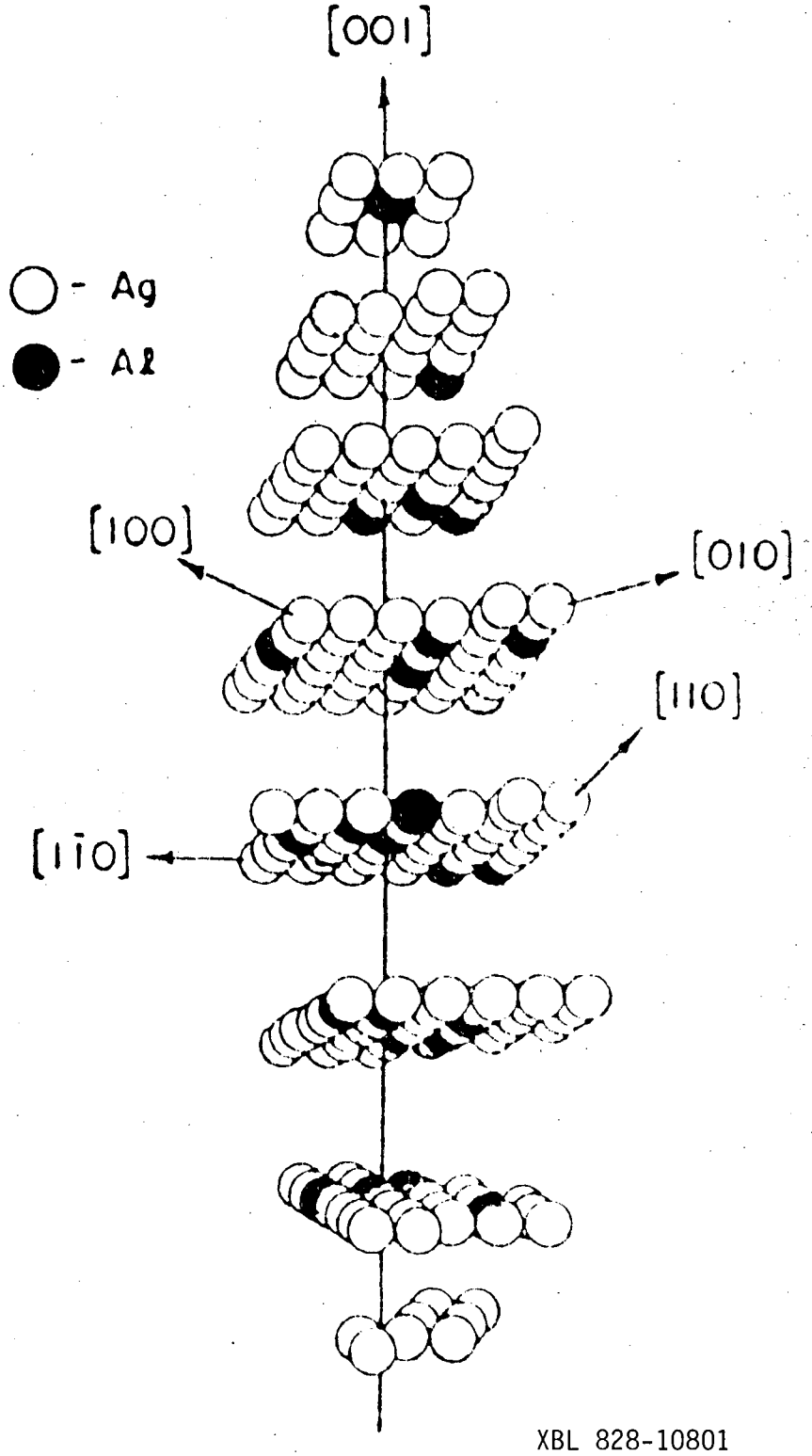


Fig. 2a

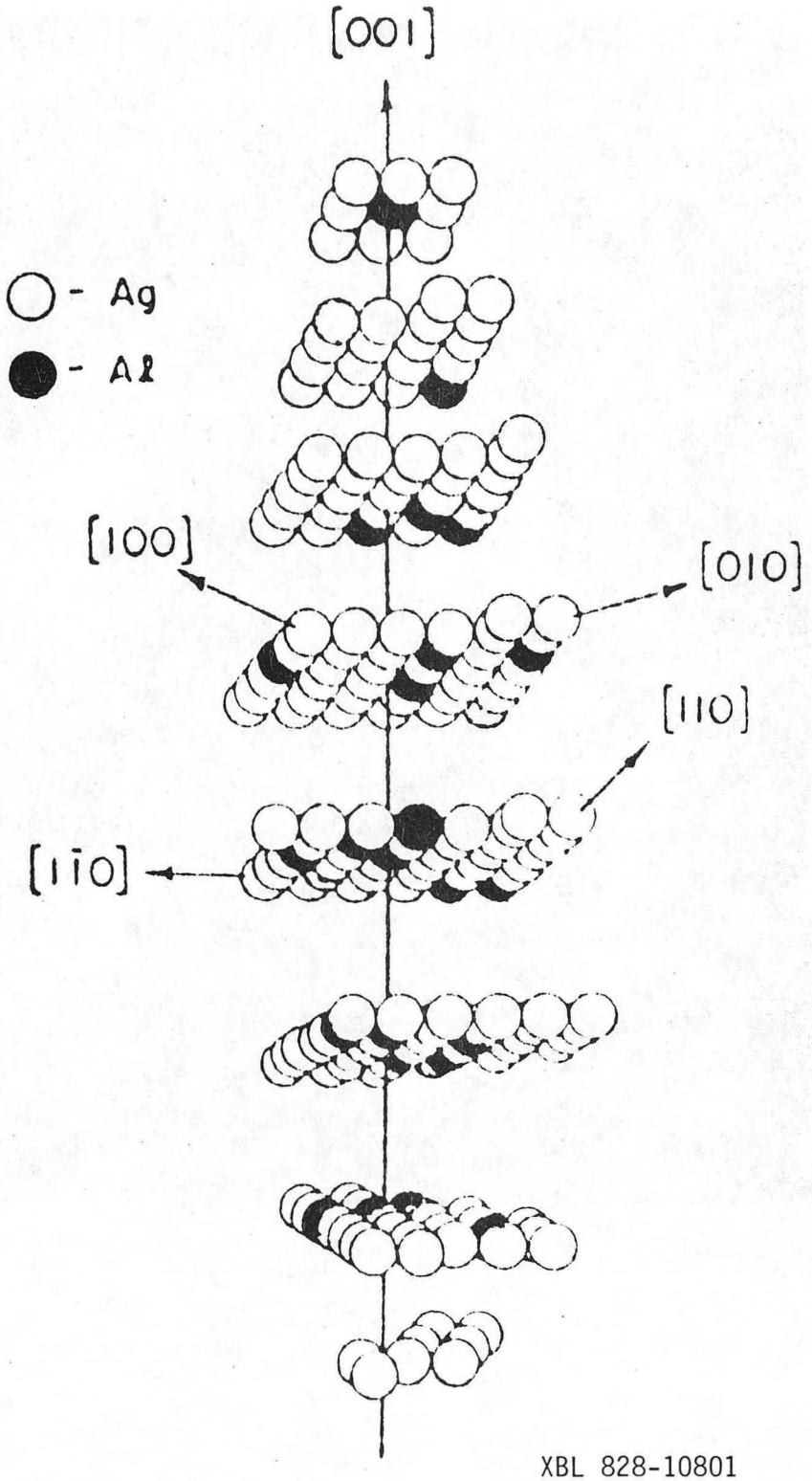


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Fig. 2a

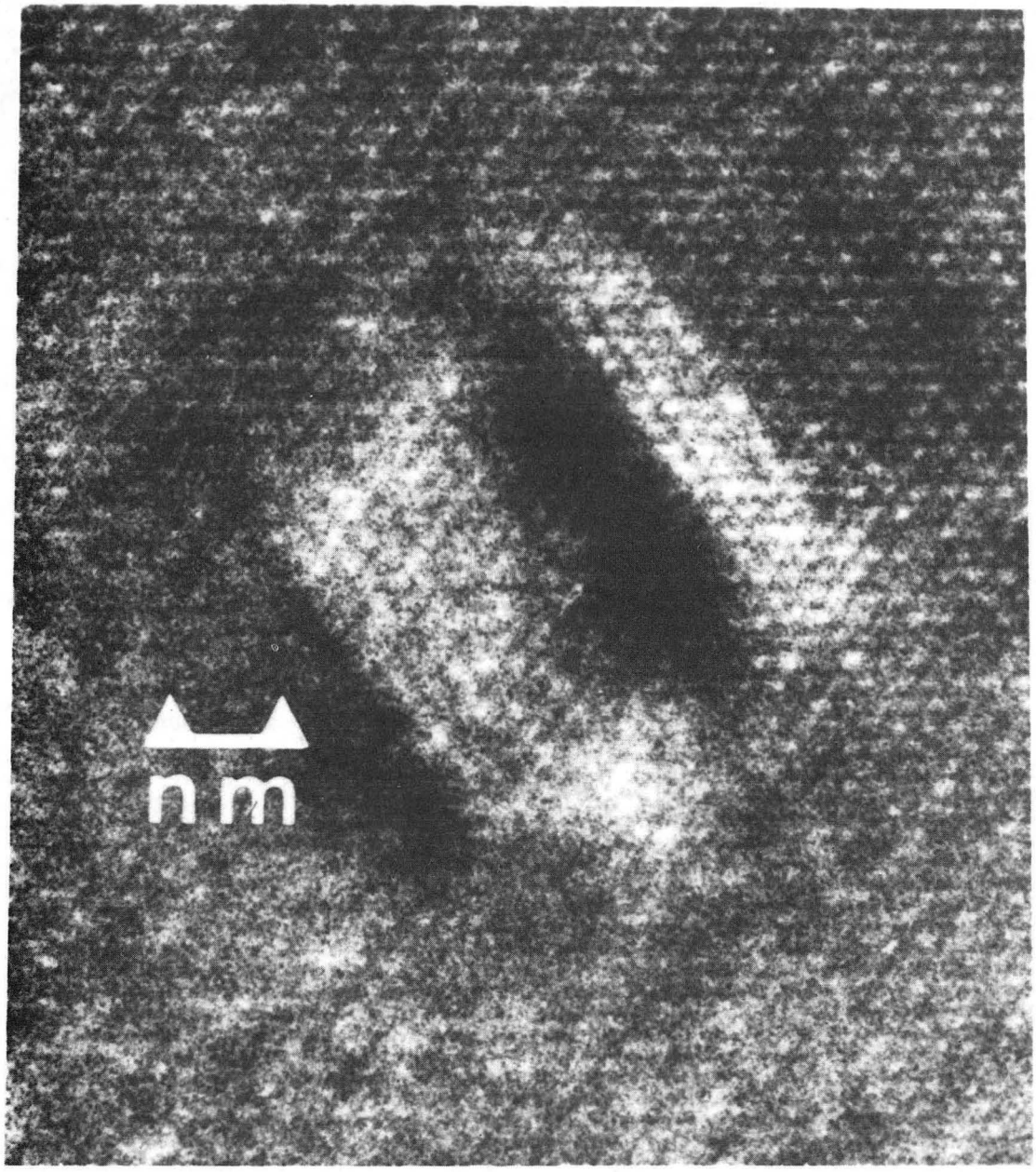

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Fig. 2b

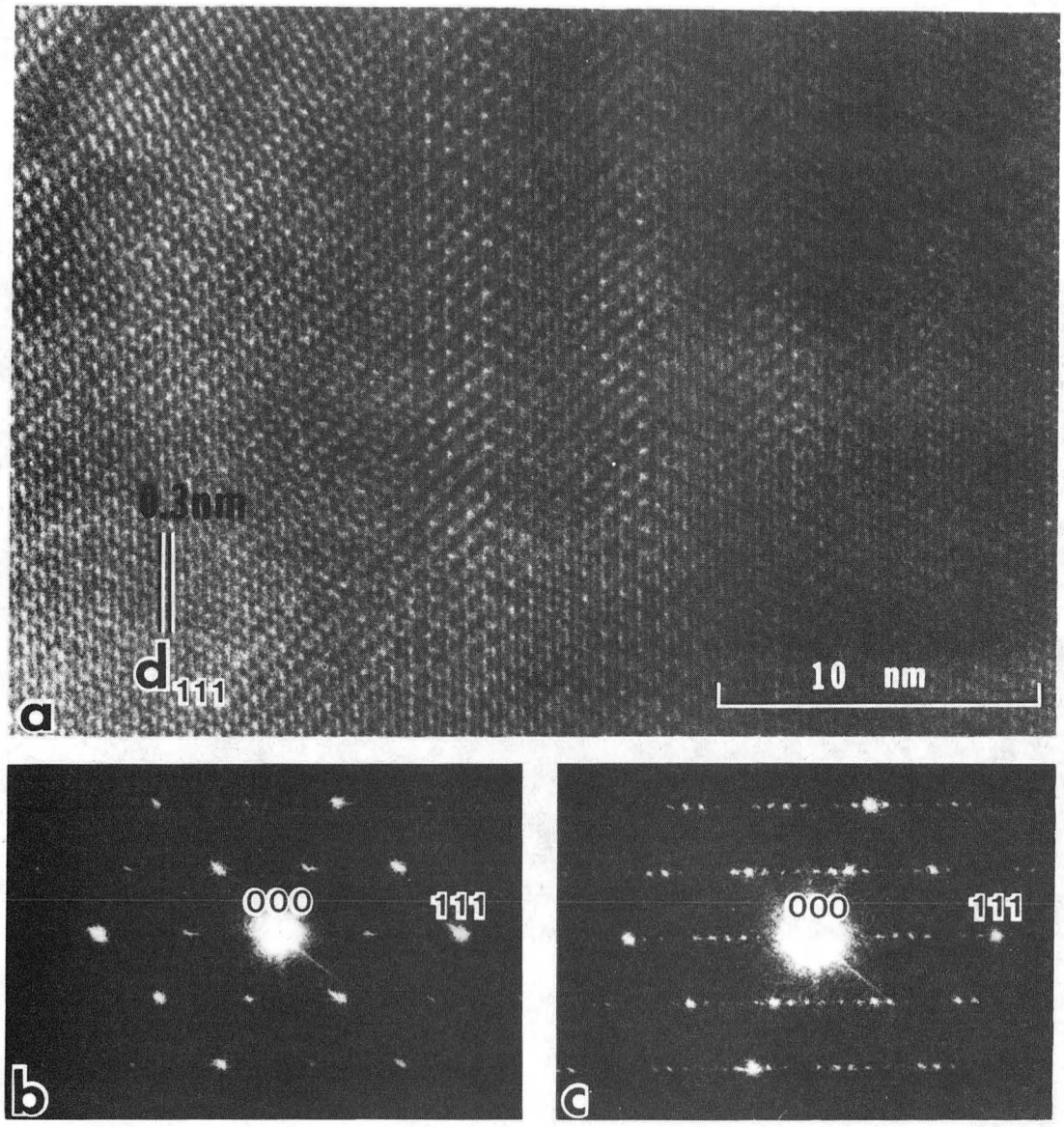

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Fig. 3

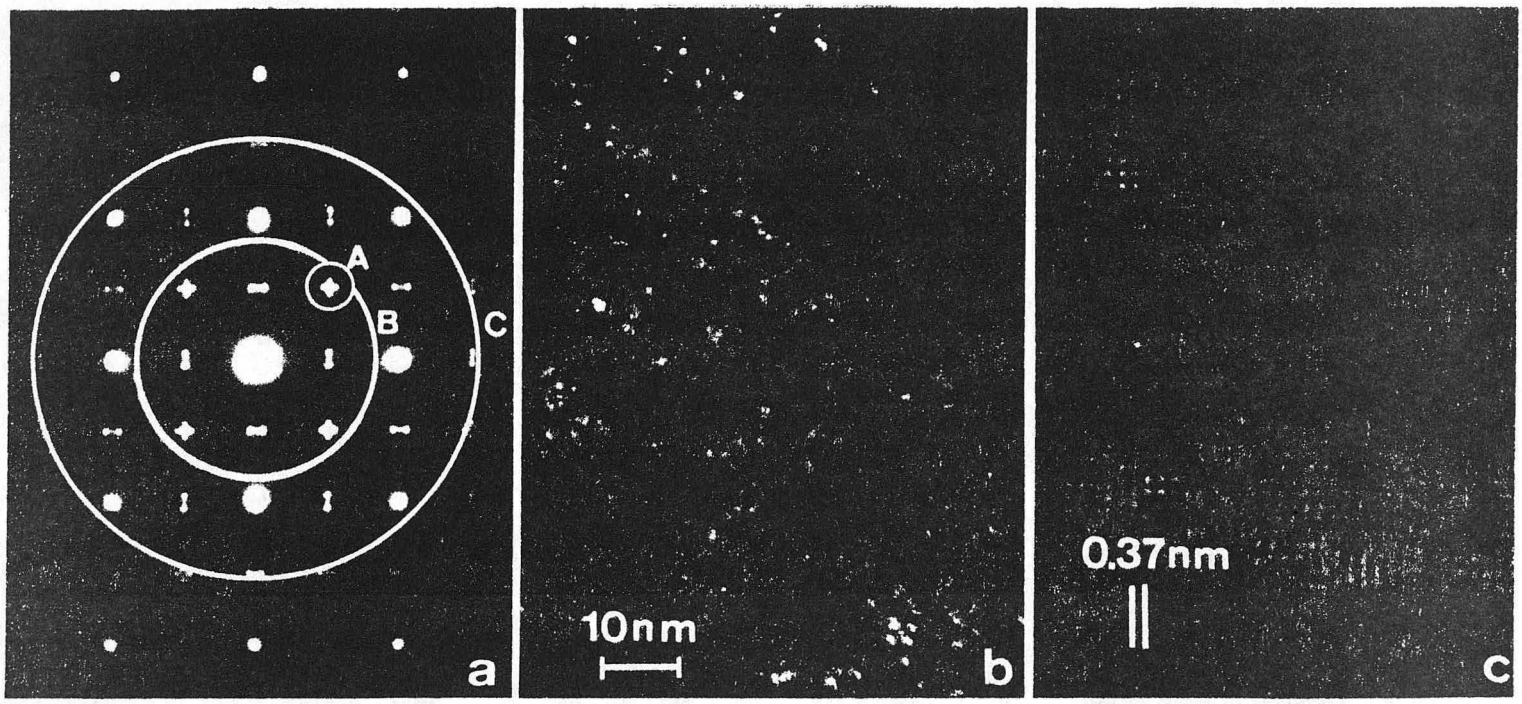

Fig. 4

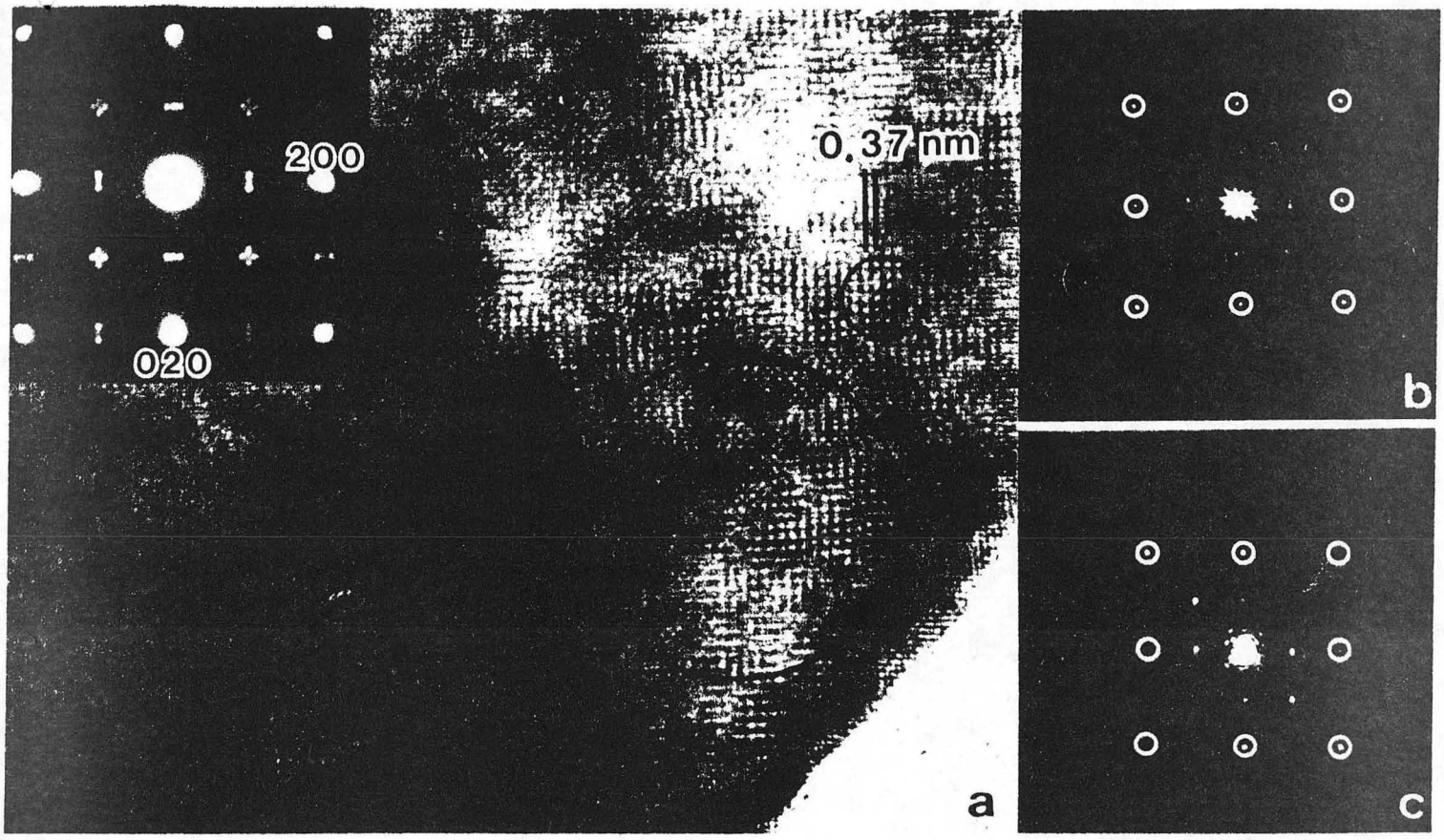

Fig. 5

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