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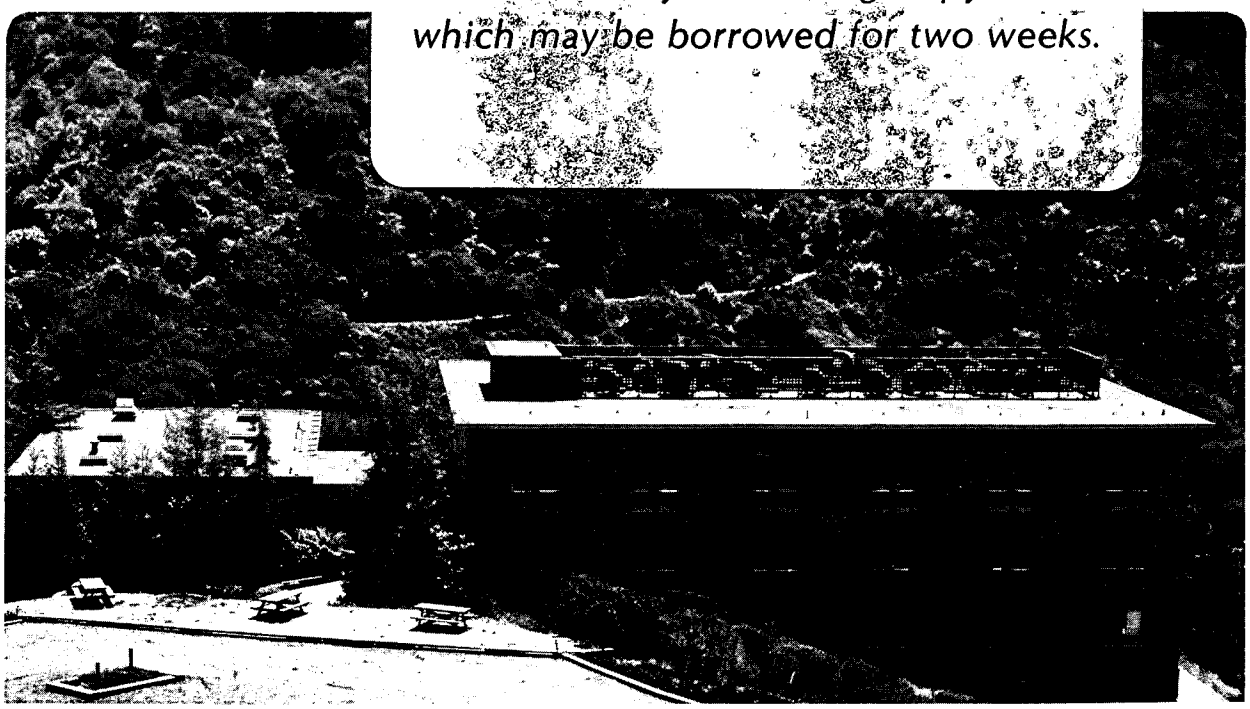

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FACTORS DETERMINING THE MORPHOLOGY OF PRECIPITATION IN ALUMINUM-GERMANIUM AND ALUMINUM-SILICON ALLOYS

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Synopsis

HVEM in-situ studies of precipitation in Al-Si and Al-Ge alloys complemented by high resolution observations have provided a clear picture of the fundamental nucleation and growth processes. A model for the role of vacancies in precipitate growth was in general agreement with a dynamic sequence recording the loss of coherency during plate growth. High resolution images obtained on the NCEM's Atomic Resolution Microscope provided direct information of precipitate/matrix interface structure, internal precipitate structure and orientation relationships. Based on the observations, simple model nuclei for various morphologies are proposed. These suggest that variations in the absolute and local vacancy supersaturation give rise to the precipitate patterns observed.

Introduction

In spite of their simplicity, aluminum-silicon and aluminum-germanium alloys are interesting systems to study. The terminal solid solubility of both Si and Ge in Al is quite limited and strongly temperature-dependent, giving rise to classical precipitation hardening behavior. In both alloys direct precipitation of the equilibrium pure Si or Ge phase occurs after an appropriate quench/age treatment. In contrast to their uncomplicated phase diagrams, the morphology of the precipitate structures as determined by transmission electron microscopy studies [1-9] is surprisingly varied. Al-Si alloys form plate, needle and lath precipitates on various habits[1], while in Al-Ge alloys similar morphologies but sometimes different habits, plus the intriguing additional morphology of tetrahedral-shaped precipitates, have been reported[5,8]. Most of the investigations find several orientation relationships and the results are generally consistent.

Some aspects of precipitation in these simple model alloys have been studied in detail, particularly the nucleation stage[10] and the indispensable role of vacancies in the precipitation process[7,9] has been verified. However, a detailed understanding of precipitate growth has been hindered by the formidable obstacle of explaining at the atomic level how the relatively open Si and Ge diamond-cubic structures can

be formed and propagated in the close-packed aluminum face-centered-cubic structure.

In the present contribution the results of recent work using both high voltage in-situ and high resolution techniques are presented and discussed in terms of provisional models that are consistent with most of the observations.

An additional motivation for embarking on this work was the expectation that any knowledge gained from studying the interface structures of Si and Ge with Al might also be applied to technologically important problems in the semiconductor field.

Experimental Details

Alloys of the material of nominal compositions Al-1a/o Si and Al-1a/o Ge were prepared from pure elements in the form of 0.1 mm foils. After appropriate quench or quench/age treatments from 540°C, thin foils suitable for microscopy were jet-polished using standard procedures. In some instances the precipitate structures were formed during aging of the bulk foils, in others by in-situ heating of the as-quenched foil in the HVEM.

For the in-situ studies a Kratos EM 1500 equipped with a Gatan heating stage and a Westinghouse ETV 1680 EBS video camera were used. High resolution imaging of precipitate needles was performed on the JEOL ARM-1000, which allowed precise alignment of the electron beam along the needle axis, regardless of the foil surface orientation. Microscope alignment procedures and the selection of suitable areas was facilitiated by the use of a Gatan 622-0600 video camera operated with a YAG scintillator.

Results and Discussion

Summary of Observations

On the basis of a large body of experimental evidence, selected examples of which will be presented here, it can be stated that in Al-Si and Al-Ge:

1) A wide variety of precipitate morphologies are developed, each with a well-defined orientation relationship and with low index planes in the two structures exactly parallel;

2) Vacancies are essential to the precipitation process and variations in the precipitate morphologies between the two alloy systems as well as within each system are related to differences in vacancy requirement and variations in the local vacancy supersaturation, respectively.

3) Precipitate morphologies reveal a marked preference for the development of $\{111\}_{Si}$ facets.

4) In most instances the precipitates are well-accommodated in the matrix, at least in the later stages of growth and they are also invariably twinned.

5) The preponderant morphology in Al-Ge alloys is $<100>_{Al}$ needles, whereas in the Al-Si it is $\{111\}_{Al}$ plates with 1/2 $<110>_{Al}$ strain fields.

6) The precipitates grow to near-equilibrium shapes in conformance with the dictates of crystal symmetries.

7) Measurements of precipitate thicknesses indicate that discrete values are favored showing that growth proceeds in fixed increments.

8) Pentagonally-twinned needles are frequently found in both $<001>_{Al}$ and $<011>_{Al}$ zone axes.

These facts, together with the work cited earlier[1-10], are now used to develop structural models for the nucleation and growth of various precipitate morphologies.

{111} Plates

Due to their more open structure, Si and Ge when they precipitate in Al, undergo a large volume expansion of 20% and 36%, respectively. Vacancies are therefore an essential ingredient in the precipitation process. Some important parameters for Al, Si and Ge are listed in Table I.

Table I

Crystallographic Data for Al, Si and Ge

	Si	Al	Ge
a_a(Å)	5.658	5.428	4.04
a_{Al}/a	0.75	0.72	
Ω(Å^3)	19.99	16.60	22.64
$\Delta\Omega$(%)	20	36	

Since it is experimentally observed that most precipitates are strain free, the lattice correspondences for these particles must incorporate vacancies in sufficient numbers to eliminate (or nearly eliminate) the volume mismatch. The search for lattice correspondences is thus reduced to looking for near-coincidence site lattices made of

integral multiples of both lattices. The smaller the repeat unit and the smaller the residual distortions needed to bring the nearly coincident lattices into exact coincidence, the higher the physical significance of a lattice correspondence. It is always possible to find an arbitrarily close fit between two lattices given large enough corresponding cells. However, physical precipitation is governed by those correspondences that have small repeat distances.

Al-Si

For Si precipitation in Al it has been recognized that every three unit cells of Si (3 x 5.43Å) are nearly coincident with every four unit cells of Al (4 x 4.05Å)[11,12]. An elastic distortion of 0.5% will bring these two corresponding units into exact coincidence. This correspondence implies that 256 lattice sites in a four unit cell cube of Al transform to 216 lattice sites in a three unit cell cube of Si, thus 40 vacancies are required. Using the primitive cell of this lattice correspondence, one in 64 Al atoms is in exact coincidence with one in 54 Si atoms, requiring 10 vacancies. Figure 1a illustrates one close-packed plane in this correspondence with coincident sites (marked) at the corners. The two levels of atoms in the Si {111} plane are shown as atoms of two different sizes. The level of the larger ones is exactly coincident with the Al {111} plane. The transformation strain is a pure dilatation, and with the matrix being the elastically softer phase a spherical particle shape would minimize the strain energy. Of the observed morphologies, that of the tetrahedron, which is reported to be present in Al-Ge aged at 200°C[8], is closest to a sphere. However, most particles that follow a cube/cube orientation relationship are plates[5,13]. This morphology is plausible because vacancies necessary to accommodate the volume change are known to "precipitate" in Frank loops on {111} planes in Al. Moreover, the density of atoms in equivalent atomic planes is similar in Al, Si and Ge, because Si and Ge fortuitously have lattice parameters that are close to $\sqrt{2}$ times that of Al. As a result a close-packed plane of the Al lattice could transform into a close-packed plane of the Si (Ge) lattice by a simple atomic rearrangement, leaving the coincidence sites unchanged. The more open structure of the precipitate will result in an expansion normal to the plane which must be accommodated by a layer of vacancies on every fourth {111} Al plane. Thus a credible nucleation event is one in which solute atoms and vacancies coprecipitate on $\{111\}_{Al}$ planes.

A similar mechanism has been inferred to occur in other alloy systems where there is a large disparity in the size of the parent and product phases[14]. A <110> projection of such a nucleus is shown in Fig. 1b. If it grows laterally or in thickness by adding the correct number of vacancies to maintain a 4:3 ratio of Al to Si planes, the remaining strain t

o be accommodated elastically is a 0.5% uniform expansion. If, on the other hand, the supply of vacancies is insufficient, growth might proceed conservatively without the aid of vacancies. As shown by arrows in Fig. 1b, a {111} plane of the Al lattice when it transforms to a {111} double plane of the Si lattice, suffers a displacement of ≅1/6<110>. Thus after three layers this displacement is ≅1/2<110> in agreement with the experimental observation. Apparently this displacement is large enough to stop further growth until an additional layer of vacancies or a matrix dislocation arriving at the interface has relieved the strain.

The unit cell of the coincidence site lattice shown in a {111} section in Fig. 1a and in <110> projection in Fig. 1b illustrates the 4:3 match between the two lattices. The coincidence site cell is two <110> vectors in edge length and the corresponding DSC lattice[15] is made up of 1/6<110> vectors, as shown in Fig. 2. Nonconservative precipitate growth leaves the CSL undisturbed, while conservative growth corresponds to a DSC lattice displacement and will shift the CSL, producing a CSL stacking fault. It is interesting to note that three different 1/6<110> displacements can be associated with the conservative transformation of a {111} close-packed plane. Each will cause a different CSL shift, and will give rise to a different 1/2<110> displacement vector. This is entirely equivalent to the three different partial dislocations that can cause the same stacking fault in fcc materials. For a given {111} plate one of the three possible <110> prismatic displacement vectors will develop during a growth increment. In the absence of excess vacancies or a sufficiently high temperature further growth will be inhibited unless the coherency strains are relaxed by incorporating a matrix dislocation into the matrix/ precipitate interface. Dislocations with 6 of the 12 possible 1/2<110> Burgers vectors will be effective for this purpose provided the dislocation is free to glide and climb around the precipitate periphery.

Direct evidence for this process and the subsequent propagation of a series of growth ledges was obtained during in-situ heating of Al-Si. Figure 3 shows a series of micrographs taken from a video recording of such a heating sequence. Dislocation contrast is seen whenever the displacement reaches 1/3<110> and 1/2<110> but not at 1/6<110>[16]. Displacement contrast occurs for all precipitate thicknesses that are not an integral multiple of Al{111} spacings. All the different stages of growth can be discerned in Fig. 3, for the plate marked A. Other plates exhibit similar behavior and partial or complete growth sequences can be seen for plates B, C and D. In some instances more complex dislocation reactions and incomplete envelopment of the precipitate lead to a less clear result An ideal growth sequence and subsequent loss of coherency is schematically illustrated in Fig. 3b. A comparison with the experiments of Fig. 3a (particularly when the original video tape is viewed) shows excellent agreement. Further

support for this growth model was obtained earlier, when it was shown that similar loss of coherency of a {111} plate occurs when electron-irradiation induced interstitial loops nucleate and grow in the matrix adjacent to a precipitate[3,7].

Figures 1a and 1b show the smallest repeat unit of the lattice correspondence. Notice that two faces of the Si unit in each figure have atoms with three dangling bonds. Assuming that the bonding requirements at the Al/Si interface are determined by a criterion of minimum number of dangling bonds it is more likely that a nucleus will be bounded by {111} faces with only single dangling bonds, as drawn in by dashed lines in Figure 1b. This nucleus is not a repeat unit of the CSL and it requires fewer vacancies than a full repeat unit would.

Even fewer vacancies would be required if the nucleus were shaped like a tetrahedron as shown in Figures 4a and b. It may thus be possible that the different particle shapes and orientation relationships are closely linked to local vacancy concentration during nucleation. This is all the more likely as it is clear that during strain-free growth the same number of vacancies is required for all particle shapes and orientation relationships. In Fig. 5, taken from a foil aged in-situ, a comparison of the frequency of different particle morphologies in Al-Ge, near the free surfaces (a), near a grain boundary (c), and in the bulk (b) shows that needles are most prevalent in regions of relatively low vacancy concentration, followed by plates in intermediate vacancy concentrations, followed by a uniform mixture of all particle shapes in the bulk. The morphology of precipitates thus appears to be a finely tuned balance of different nuclei stable under varying conditions.

Al-Ge

The arguments used to develop a model for the nucleation and growth of {111} plates in Al-Si apply equally well to Al-Ge, differing only in the numerical values for the CSL. In this case 1372 lattice sites in a seven unit cell cube of Al transform to 1000 lattice sites in a five unit cell cube of Ge.

<100> Needles

A striking aspect of the observations in Al-Ge was the frequent occurrence of high aspect ratio needles lying in <100> matrix directions. Typical examples are seen in Fig. 5. Figure 6 shows a high resolution image of such a needle or lath seen end-on. The orientation relationship is <100>Al||<110>Ge along the needle axis and <001>Al||<111>Ge normal to it[17]. The particle is facetted on {111}Ge planes and exhibits internal twins parallel to these facets. Many similar particles were examined at high resolution and it was found that most followed the same orientation relationship

whose monoclinic symmetry was reflected in the particle shape[18,19]. This observed symmetry suggested that the particles grew to near equilibrium shape. Without exception all such particles exhibited internal twins, and often it appeared as though the {111} plane in contact with the matrix was faulted, as seen for example in Fig. 6. The same morphology and orientation relationship was observed in Al-Si alloys but much less frequently.

An explanation for these observations is suggested in Fig. 7, which shows a plausible nucleus of a <100> needle in Al-Ge. As before this is not a repeat unit since it is bounded by two complete {111} double planes, minimizing the number of dangling bonds. The reason for the ubiquitous twinning is clear from this twinned nucleus; it is required to improve the match between the two crystals by incorporating a mirror plane in the nucleus parallel to the mirror plane in the matrix. The residual mismatch, to be accommodated elastically, is 1.2% along the needle axis, and 0.8% and 2.7% in the plane normal to the needle axis. As seen in Fig. 7, the CSL of such a nucleus is very small and since it consists of only two {111} double planes its formation requires a minimum number of vacancies.

Although the same is true in Al-Si the residual strain along the needle axis is much larger (5.2%) than for Al-Ge. This explains why <100> needles are rarely seen in Al-Si alloys and emphasizes again the delicate balance of nucleus shape, residual strains, and vacancy concentration. Note that due to its larger (36%) volume expansion Ge needs almost twice the vacancies required for Si (20%), which explains why needles are the favored morphology in Al-Ge and plates in Al-Si.

When a nucleus such as the one shown in Fig. 7 grows it must do so non-conservatively, incorporating an equilibrium number of vacancies. For a Si nucleus in cube-cube orientation this was shown earlier to be the case for a 3:4 Si:Al match with a 0.5% residual expansion. The equivalent for Ge is 5:7 Ge:Al with a very small residual mismatch (0.2%).

Pentagonally-Twinned Needles

In addition to the normal multiple twinning invariably associated with $<100>_{Al}$ needles in Al-Ge (e.g., Fig. 6), end-on observation revealed that the particles in many instances are pentagonally-twinned. Examples found in Al-Ge and Al-Si for $<100>_{Al}$ and $<110>_{Al}$ needle directions, respectively, are shown in Figures 8a and b. The particle in Al-Ge (Fig. 8a) has been discussed in detail elsewhere[19]. Multiple twinning is readily observed in end-on precipitates by conventional diffraction contrast in the HVEM and further examples, this time $<110>_{Al}$ needles in Al-Ge are seen in Fig. 9. In each case the

twinning emanates radially from a central point, again suggesting the importance of a twinned or multiply-twinned crystal as the nucleus. A possible reason for the formation of a pentagonally-twinned needle not yet explored is that nucleation of the first unit with pentagonal symmetry requires an even lower vacancy concentration than a singly-twinned nucleus.

Conclusions

1) Decomposition of Al-Si and Al-Ge alloys occurs initially by the coprecipitation of vacancies and solute atoms.

2) Variations in the total and local vacancy supersaturation lead to the development of different precipitate morphologies.

Acknowledgements

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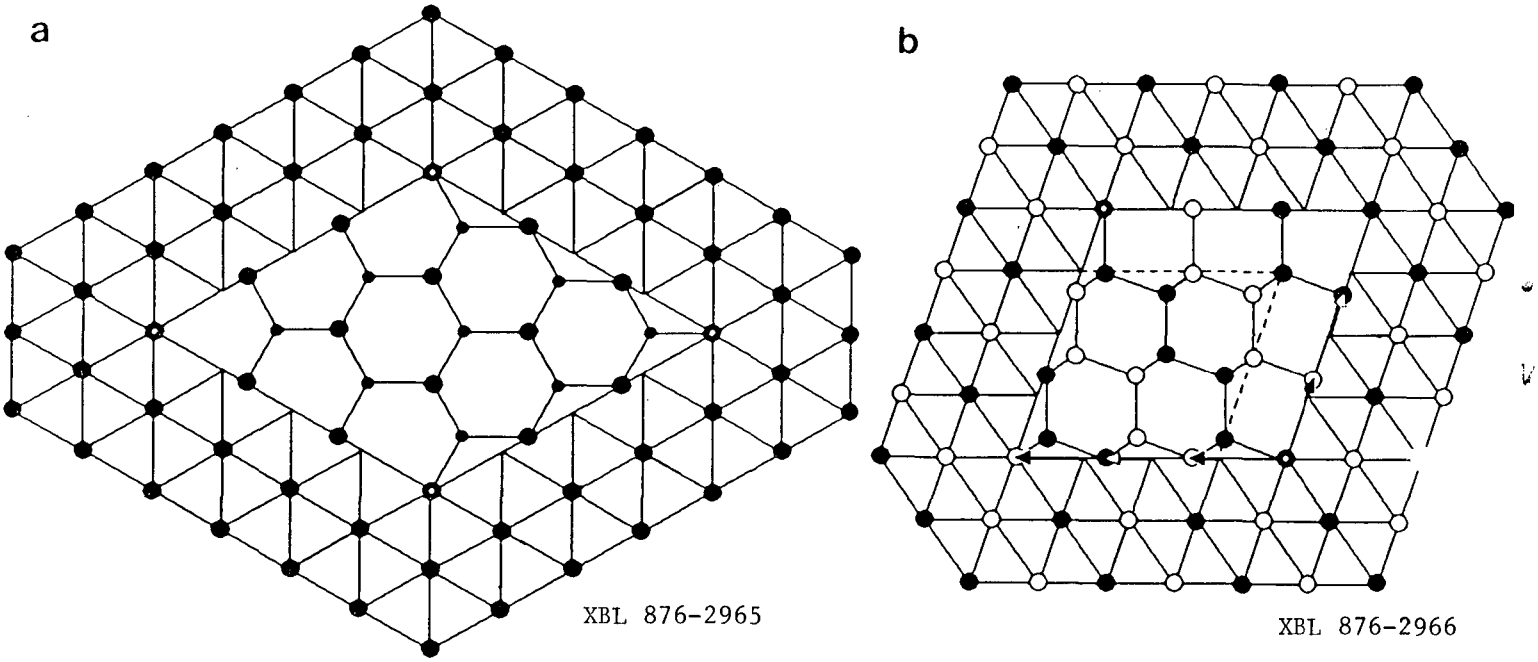


Fig. 1(a). {111} Double layer of silicon (different dot sizes mark atoms in upper and lower elevations of double layers) in a layer of aluminum illustrating the good 4:3 Al:Si matching in <110> directions.

(b). <110> projection showing the stacking of {111} planes in the Al matrix and Si precipitate. The nucleation of such a precipitate is probably initiated by the coprecipitation of vacancies and silicon atoms on $\{111\}_{Al}$. Open and solid circles denote atoms in alternating {110} layers.

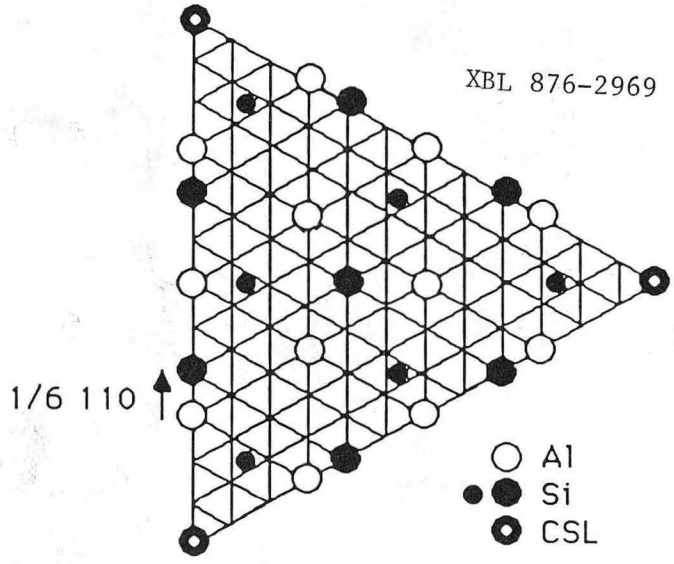


Fig. 2. {111} section showing half a cell of the Al/Si coincident site lattice and the DSC lattice (fine grid).

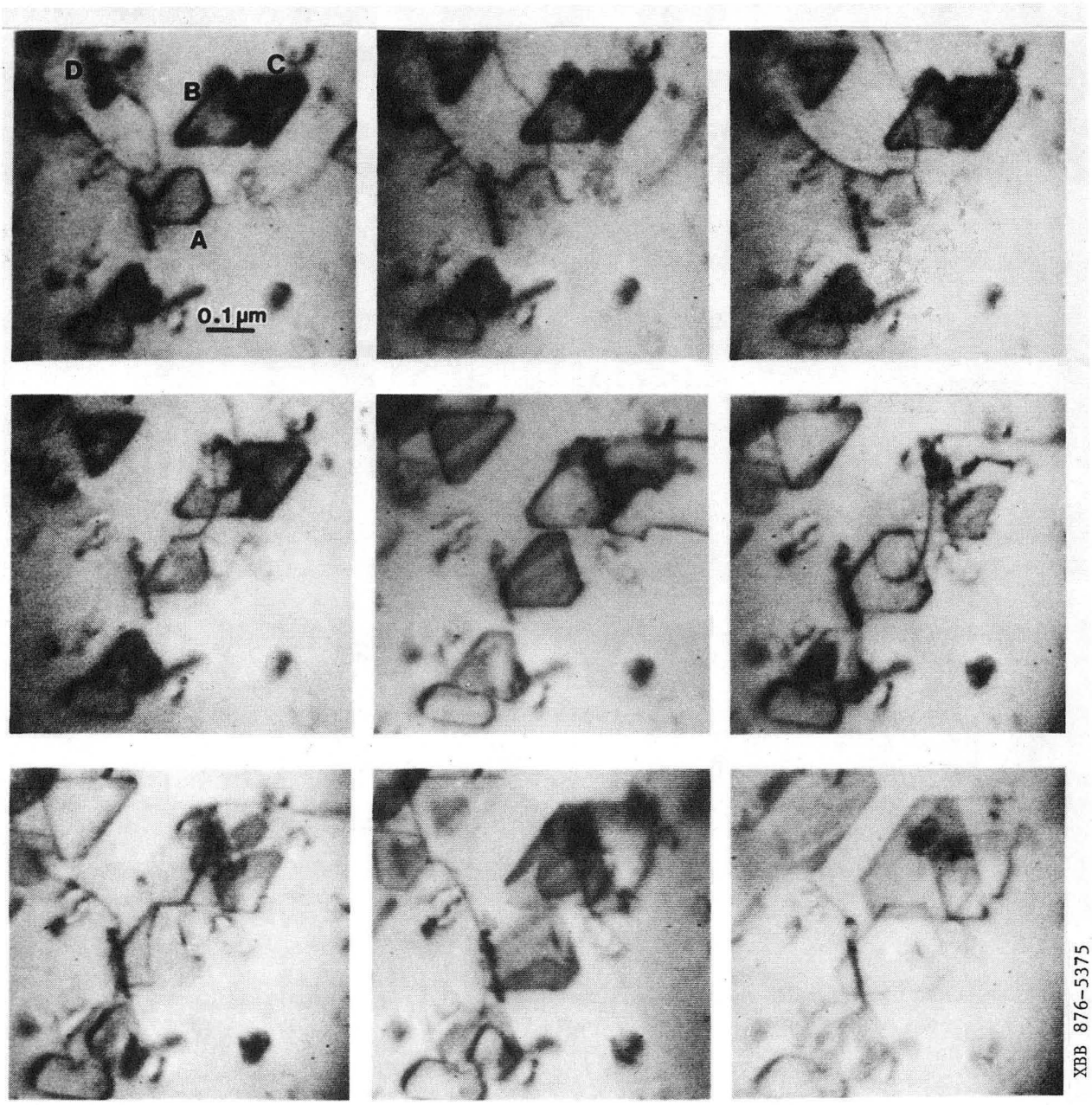
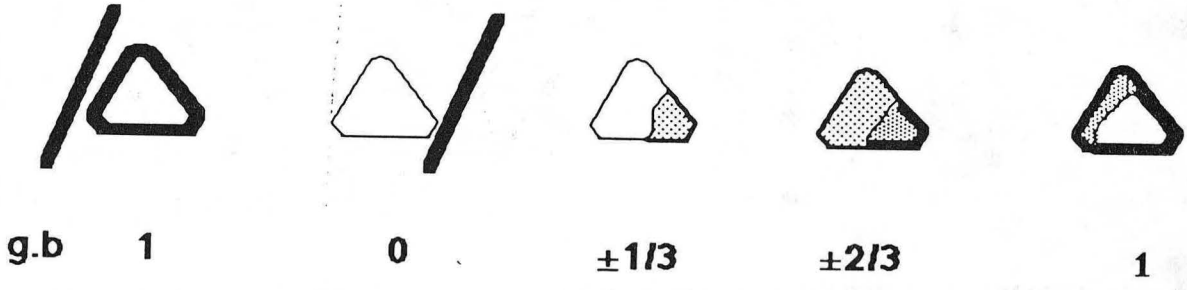


Fig. 3(a). Sequence of micrographs taken from a video tape that illustrates the loss of coherency of {111} precipitate plates in Al-1a/o Si resulting from interaction with a matrix glide dislocation. The strong 1/2<110> strain contrast initially exhibited by plate A disappears as the dislocation is incorporated in the interface. Subsequent thickening of the plate is manifested by changes in the displacement contrast in the plate interior as ledges propagate and the progressive development of contrast at the plate periphery as the ledges fully expand across the face.



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(b). Schematic diagram showing the progressive changes in structure and contrast (g.b. and g.R. values) following loss of coherency induced by interaction of the plate with a 1/2<110> dislocation.

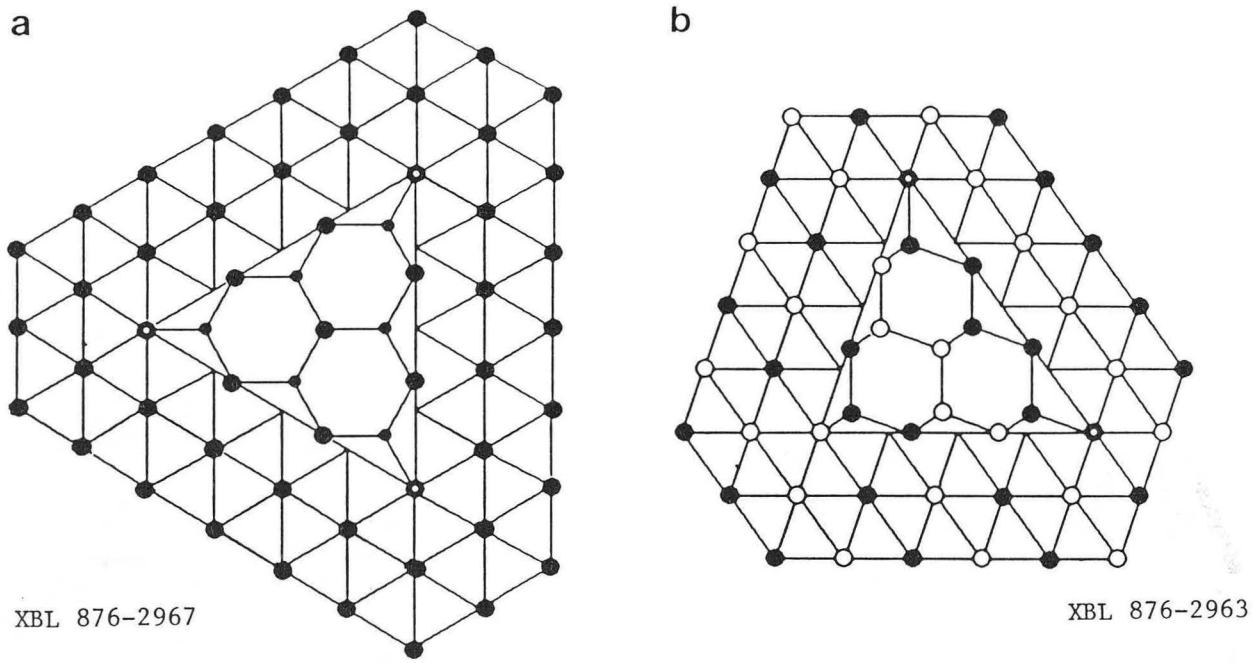

Fig. 4. Schematic showing the excellent fit of a tetrahedron-shaped Si precipitate in the Al lattice. A {111} section is shown in (a) and<110> projection in (b).

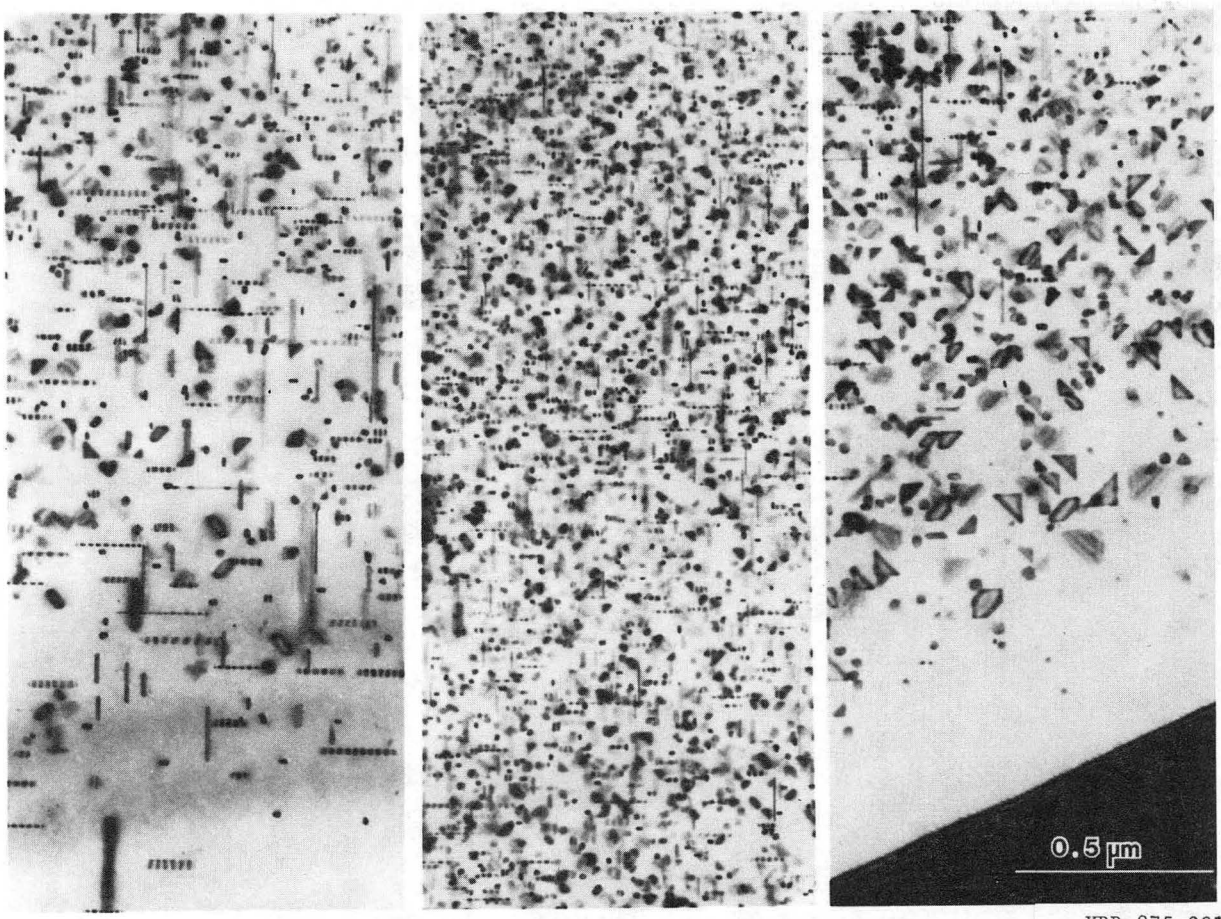

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Fig. 5. Series of micrographs taken from the same grain of an Al 1a/o Ge foil aged in-situ. The distribution and frequency of precipitate morphologies reflect variations in vacancy supersaturation; in regions near the edge of the foil mostly needles are formed (a).

In thick interior regions equal numbers of needles and plates nucleate (b) and near grain boundaries the plate morphology predominates (c).

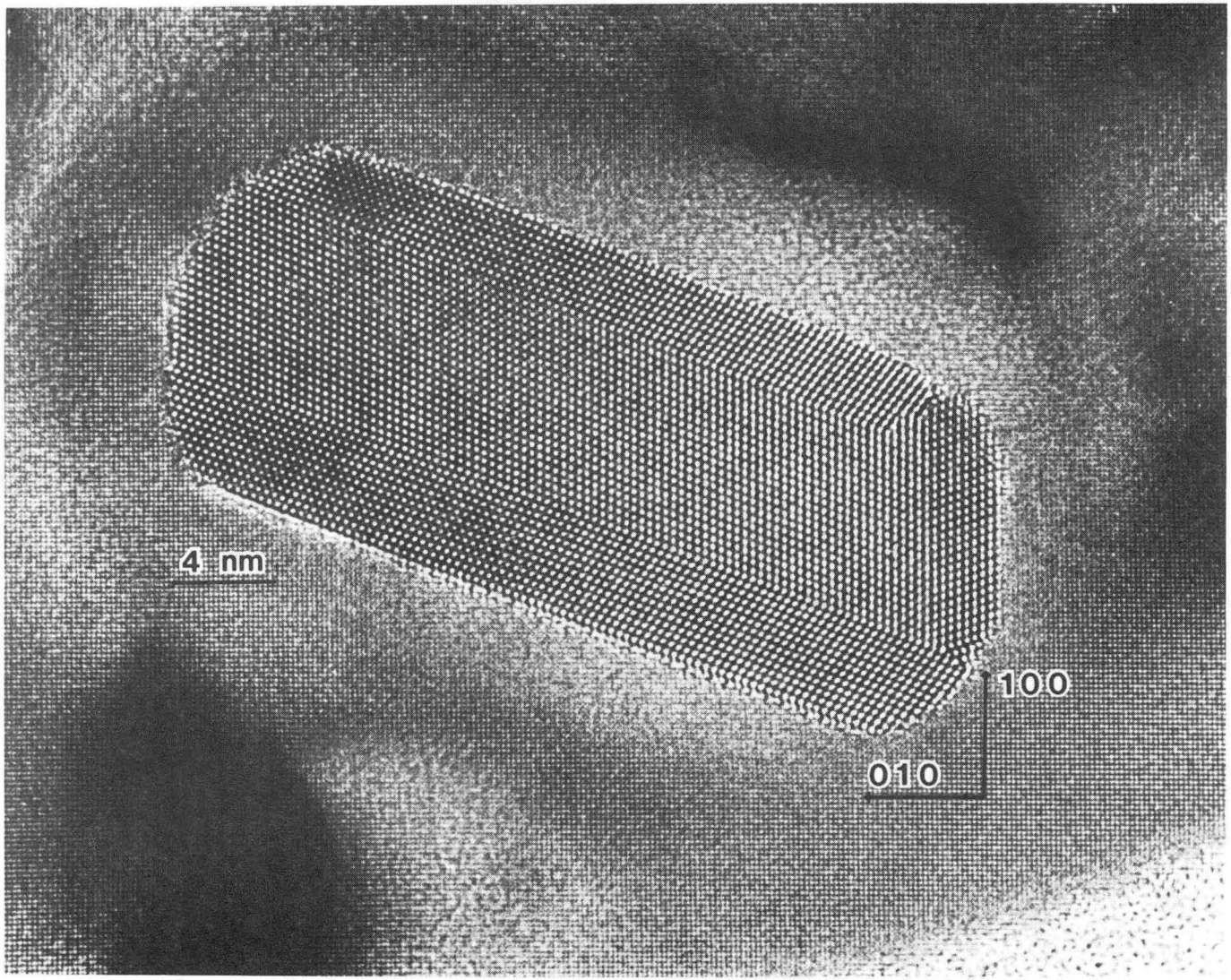

Fig. 6. A high resolution structure image of a<100> needle of Ge in Al. Several features are noteworthy, e.g., the precision of the orientation relationship along the axis, $<110>_{Ge} || <100>_{Al}$ and in the plane $\{100\}_{Al} || \{111\}_{Ge}$, the internal twinning, the good accommodation of the precipitate in the matrix, and the interface structure. (Courtesy of MRS). XBB 860-8555A

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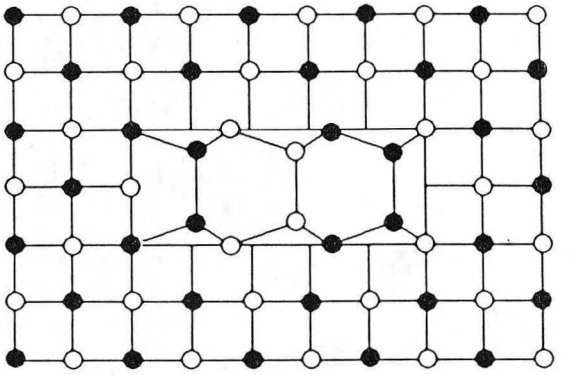

Fig. 7. Schematic diagram of the simplest plausible twinned Ge nucleus in Al showing the excellent atomic matching and the small vacancy requirement. Open and solid circles represent atoms in alternate layers.

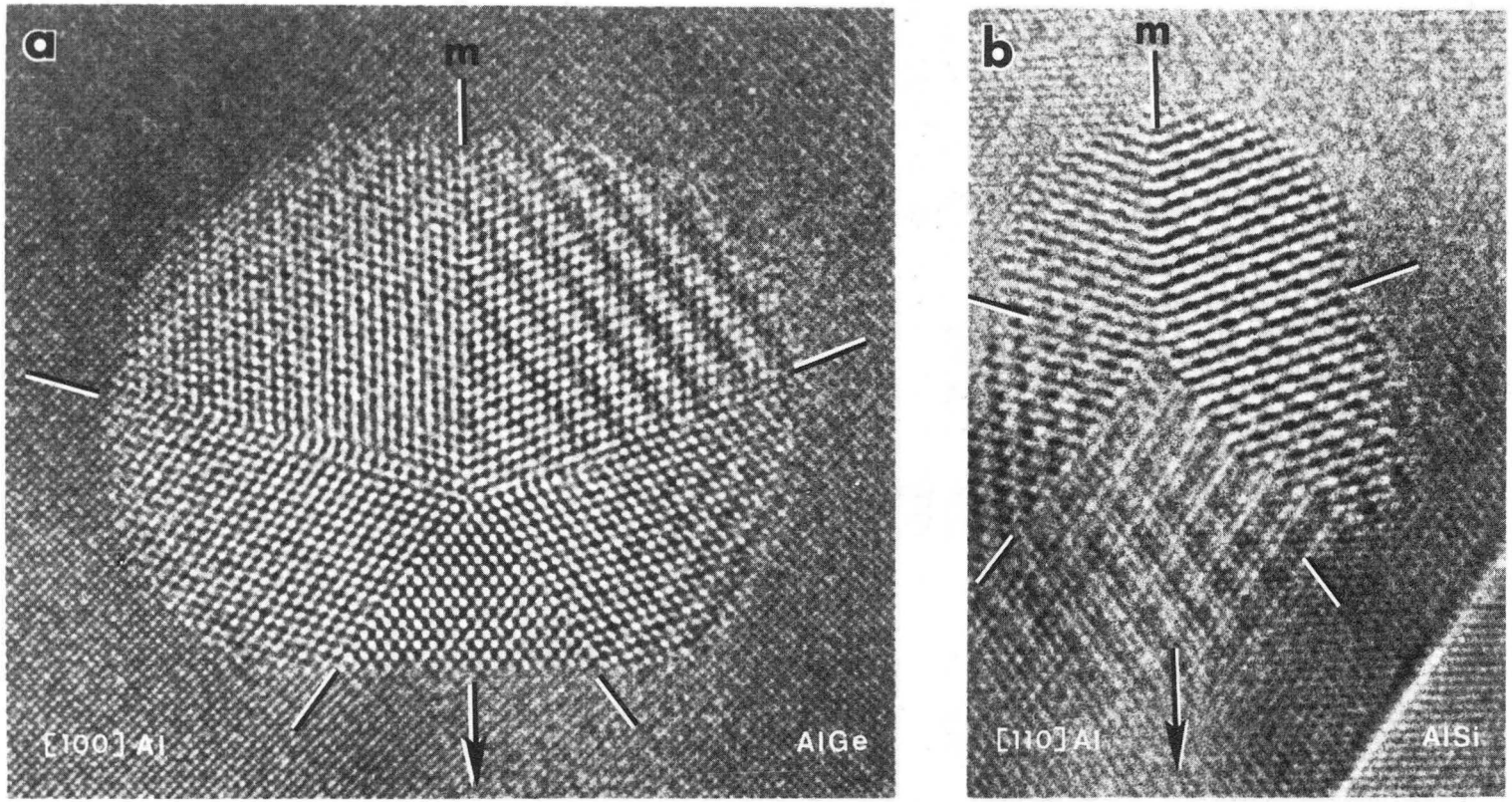

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Fig. 8. Examples of pentagonally-twinned particles found in Al-Ge (a) and Al-Si (b). (Figure 8a courtesy of Science).

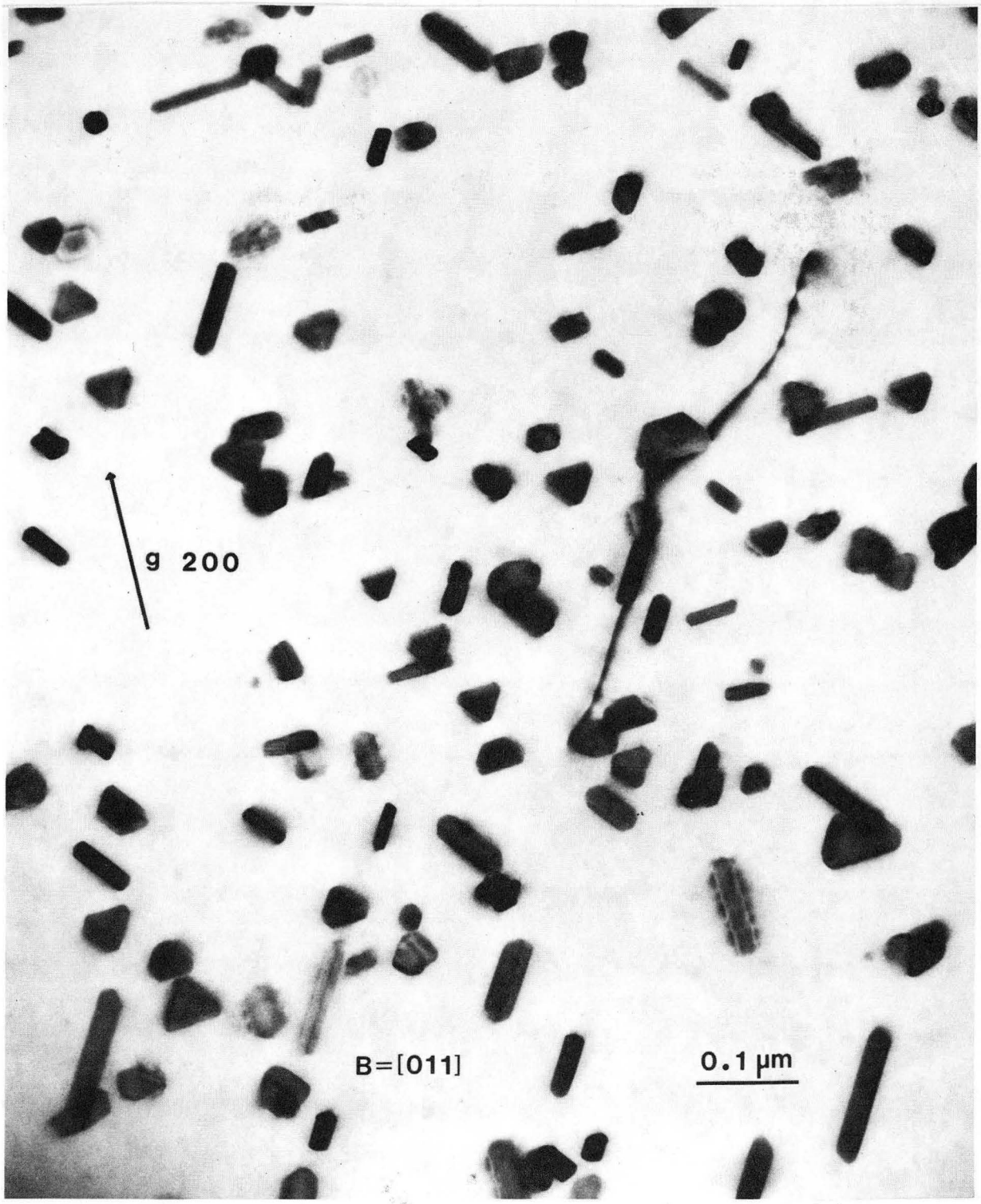

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Fig. 9. Conventional diffraction contrast HVEM image showing pentagonally-twinned particles A in a $<110>_{Al}$ zone in Al-Ge. Note the different cross-sectional shapes compared with Fig. 8(a) and (b); also the tendency for the {111} plates, B, to adopt discrete thicknesses

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