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Electron Microscope Studies on a Quenched Fe—Mo Alloy

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An alloy of Fe–Mo (50 atom%) quenched from the melt was studied using a high-resolution electron microscope. Three phases were frequently identified, *viz*, the σ-phase, the μ-phase, and the *P*-phase. The latter two were found to be rich in planar defects of intergrowth and twin type. The resolution obtained was better than 4 Å, as shown with calculated images. It was possible to derive the detailed atomic structure of the defects observed.

In alloy systems of transition elements the so-called tetrahedrally close-packed phases are common. They have complex crystal structures, and in order to understand the mechanism of formation of these phases, we recently examined relationships between their structures (*1*). Possible building blocks and defects were also discussed.

The high-resolution electron microscopy technique has been very useful in the study of the real structure of alloy crystals. So far such well-defined compounds as Ru_4Si_3 (*2*), V_4As_3 (*3*), and Mo_2BC (*4*) have been examined.

When two transition metals are melted together, the X-ray powder diffraction pattern of the quenched alloy often contains diffuse, broad lines. Traditionally such samples are heat-treated at lower temperatures to obtain crystalline order, and to facilitate phase analysis, single-crystal, and structure studies. Indeed, a direct study of the quenched alloy would be a great advantage when proposals of crystals formation like those of Ref. *1* are going to be experimentally tested. Therefore, high-resolution electron-microscopy work was started on a sample of the Fe–Mo system, which earlier was reported to contain the σ- and the μ-phase (*5*).

Experimental

A pressed pellet of molybdenum and iron in the mole ratio 1 : 1 was melted in an electric arc furnace. The pellet rested on a strongly water-cooled copper base, giving a high cooling rate. The quenched boule was crushed in a hardened steel mortar, and the Hägg–Guinier X-ray powder pattern is shown in Fig. 1. Holey carbon films with powdered sample were transferred to a Philips EM 400 electron microscope, equipped with a high-resolution goniometer and operating at 120 kV. Crystals of the σ-, μ-, and *P*-phases were identified in the sample and this agrees well with the X-ray powder pattern. Particles were normally studied under 10 000× magnification, and often could one particle contain several crystals of two different phases. Using selected area diffraction, one crystal in a particle was aligned after a short axis, and lattice image pictures were recorded at 440 000× magnification, using objective apertures of 70–100 μm. In order to increase resolution, and magnification, the specimen was often lifted in the objective lens (*6*). Almost always a crystal was bent, and the alignment procedure had to be repeated for different parts of the crystal. Extensive disorder was found

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FIG. 1. Hägg–Guinier X-ray powder pattern of the Fe–Mo alloy studied in this investigation.

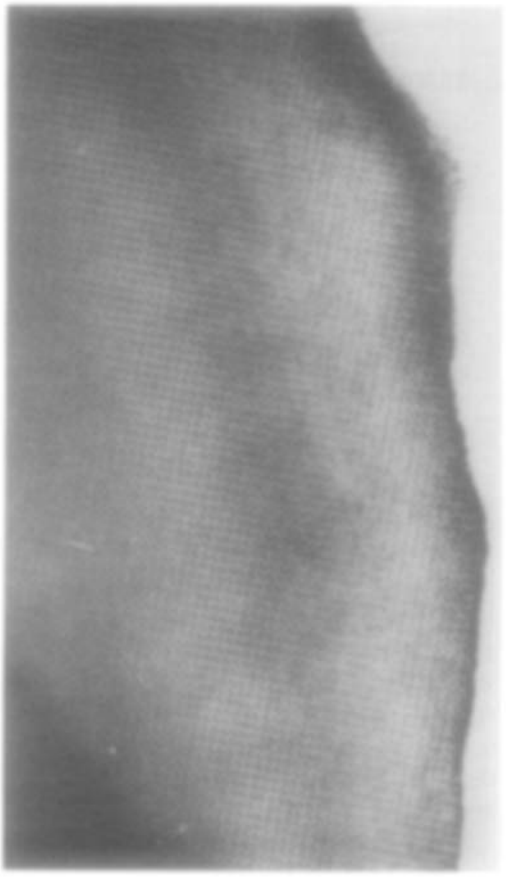

FIG. 2a. A typical structure image of a σ-phase crystal edge. Electron beam parallel with the c-axis.

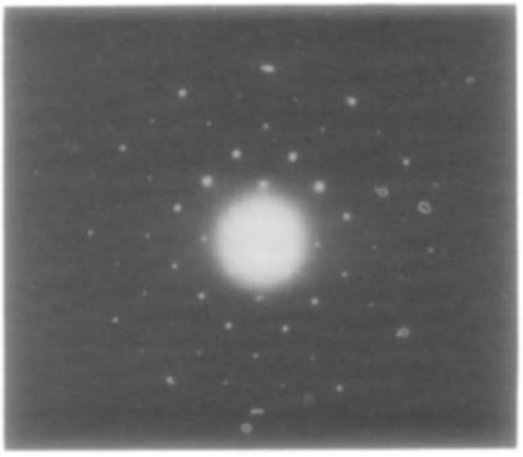

FIG. 2b. Diffraction pattern of the crystal from Fig. 2a.

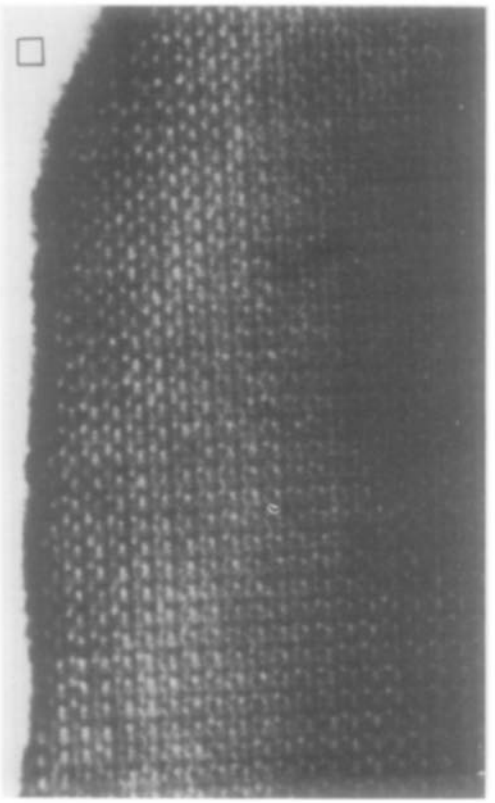

FIG. 3. Magnified part of the crystal of Fig. 2. The square in upper left corner is the tetragonal unit, $a = b = 9.2$ Å.

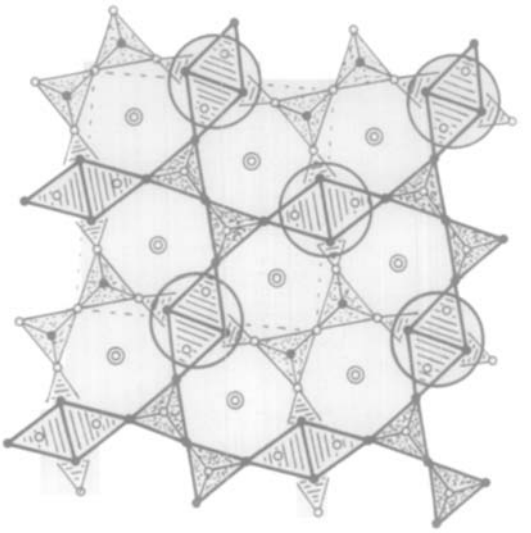

FIG. 4. The crystal structure of the σ-phase. Double circles are two atoms on $\frac{1}{4}$ and $\frac{3}{4}$. Open and filled circles atoms on 0 or $\frac{1}{2}$. Large circles correspond to white regions in the calculated image in Fig. 5.

in crystals of the μ- and the P-phases, while crystals of the σ-phase structure invariably seemed to be well ordered. Calculated images were computed using the multislice method (*7*, *8*) with a program written by P. Fejes and J. Skarnulis at Arizona State University.

Results

Several σ-phase crystal fragments were oriented so that the c-axis became parallel to the incident beam. Near the edge the crystals were transparent enough, and two-dimensional images could be recorded. A typical one is given in Fig. 2a and its diffraction pattern is given in Fig. 2b. Similar high-resolution pictures were also taken of σ-phase samples from the Mn–Cr and Fe–Cr–Si systems. Regular images were always recorded; no planar defects were observed. A magnified part of Fig. 2a is shown in Fig. 3, and the square in upper left corner is the tetragonal unit cell, $a = 9.2$ Å. The interpretation of the image follows from the atomic structure of the σ-phase, given in Fig. 4. According to Wilson and Spooner (*9*), a certain degree of ordering of the Mo and Fe atoms occurs in the σ-phase structure. This ordering should contribute to contrast in the microscope image, and various images were calculated, assuming resolutions of 2.5 and 3.3 Å, and with a crystal thickness of 30 Å. The second equal thickness contour appears (Fig. 2a) about 130 Å inside the crystal, and on both sides there are good agreement with a calculated image of a resolution of 3.3 Å and with 900 Å underfocus, as shown in Fig. 5. It is clear from these pictures that $\simeq 3$ Å atomic block resolution is present and that lattic image technique is very well applicable to alloy phases having tetrahedrally close packed structures.

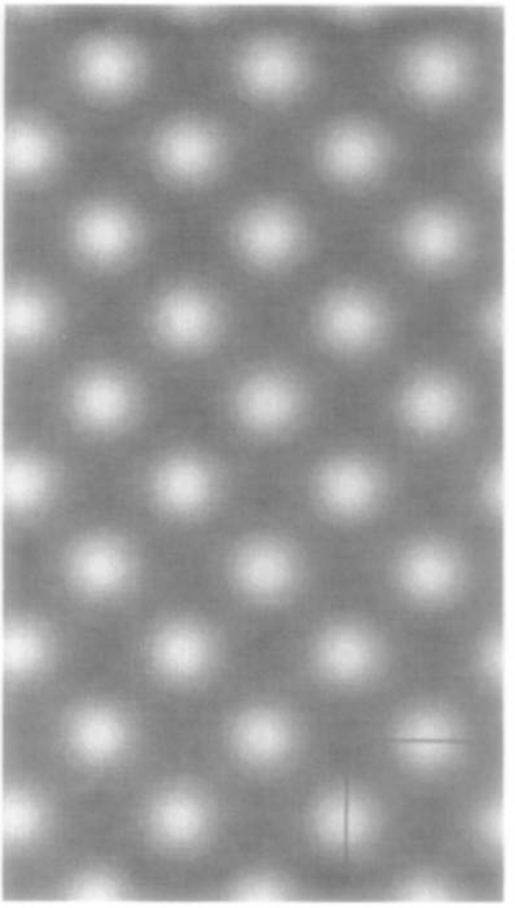

FIG. 5. Calculated image of the σ-phase.

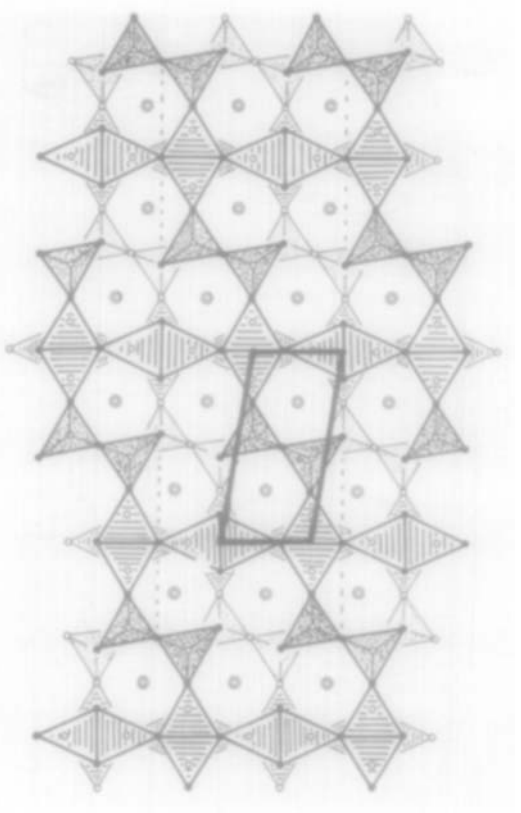

FIG. 6. The crystal structure of the μ-phase. Projection along [110]. See Ref *1* for a description of this drawing. The oblique unit given by heavy lines is resolved in images below.

The μ-Phase

The atomic structure for the μ-phase is given in Fig. 6. The structure was first determined by Westgren (*10*) and later refined for the isotypic Co_7Mo_6 (*5*). Hexagonal unit cell dimensions for Co_7Mo_6 are $a = 4.76$ Å and $c = 25.61$ Å. Four simple ways for disorder are obvious from the structure, and given in Fig. 7a, b, c, and d. Figure 7a is a twin operation, Fig. 7b is an intergrowth with a structure of Cu_2Mg type, Fig. 7c an intergrowth with a structure of $MgZn_2$ type, and Fig. 7d is an intergrowth with a structure of Zr_4Al_3 type.

Crystals of the μ-phase were frequently found in the sample. Several were aligned so that the incident electron beam was normal to the (110) plane. A typical diffraction pattern, given in Fig. 8, reveals strong disorder in the crystal. Every third layer line is sharp and a nonregular twin operation, after $\frac{1}{3}c$ (hexagonal), and shown in Fig. 7a, explains the diffraction pattern. The crystal image corresponding to the diffraction pattern is shown in Fig. 9. Fringes are invariably 8.6 Å apart, but various planar contrasts are clearly visible in the crystal. Under larger magnification a small region of Fig. 9 is shown in Fig. 10 and reveals a two-dimensional zigzag pattern. The oblique 4.1×8.6 Å unit, given in Fig. 6, is easily traced in Fig. 10, and the detailed atomic

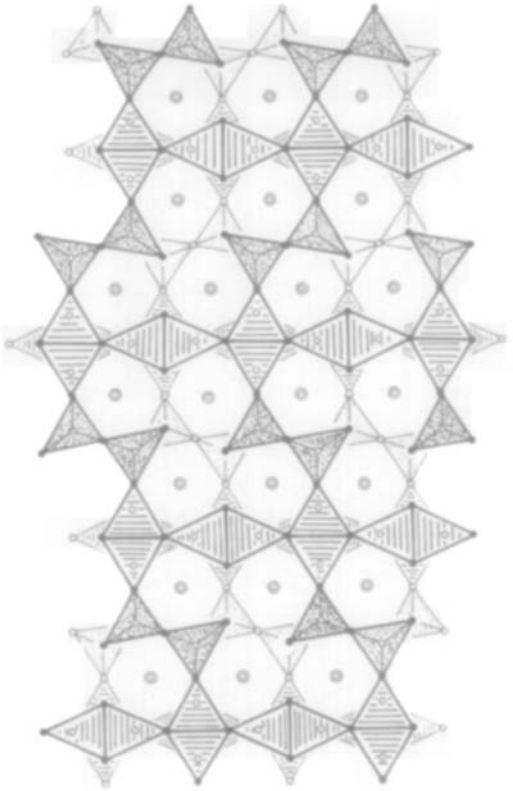

FIG. 7a. Twin operation in the μ-phase.

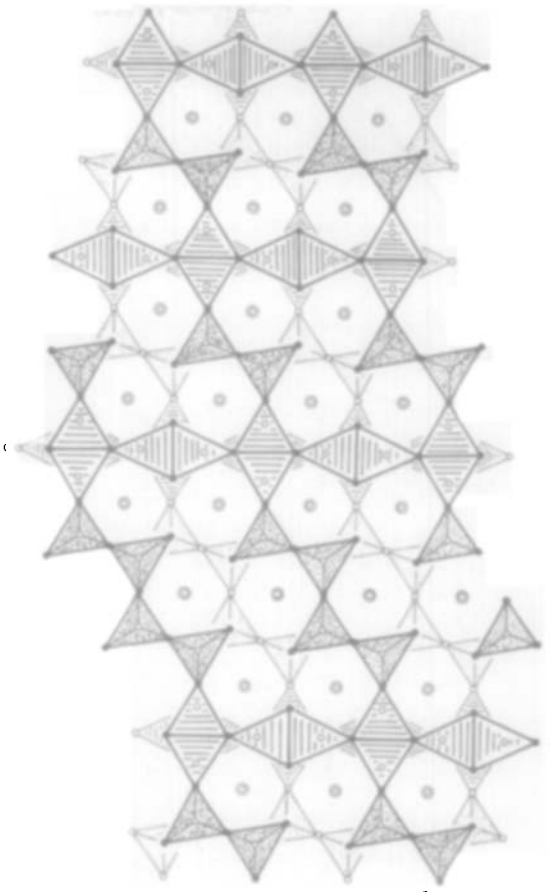

FIG. 7b. Intergrowth μ-Cu_2Mg.

structure for a region of $4\times6\times5$ oblique units, along the heavy zigzag line of Fig. 10, is given in Fig. 11. The ordering of molybdenum and iron atoms in the μ-phase does not give the same contrast as in the σ-phase, and crystals of this structure are consequently somewhat more difficult in study.

Figure 12 shows another type of planar defects in a crystal of the μ-phase. The bright fringes have a clear 4-Å resolution giving another oblique unit than the one given in Fig. 6. The angle measured from a larger magnification, given in Fig. 13, is 109°. A corresponding angle can be found in the Cu_2Mg structure; its calculated value is 109.48°. In some parts of Fig. 12, the μ-phase is also two dimensionally resolved so that the oblique unit of 4.1×8.6 Å of Fig. 6 is visible. If a part of the Cu_2Mg structure is intergrown with the μ-phase structure, as was shown in Fig. 7b the orientation of the two structures is in excellent agreement with observed images in Figs. 12 and 13. However, an ordinary Laves phase would have the composition Fe_2Mo, and the spacing between fringes should be half of what is observed in Figs. 12 and 13. The starting composition for this material was FeMo, and if ordering occurs as suggested in Fig. 14 a correct unit cell is obtained. Lattice images were now calculated with this FeMo structure, using Cu_2Mg parameters, and one at

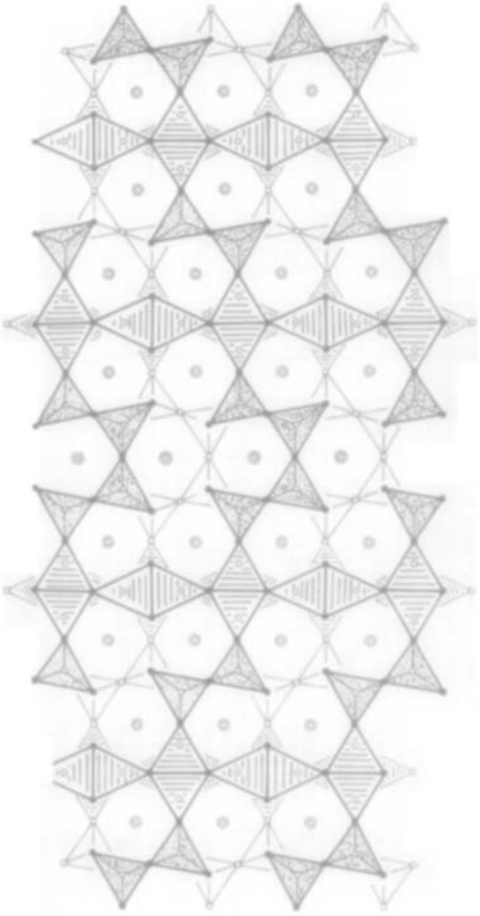

FIG. 7c. Intergrowth μ-$MgZn_2$.

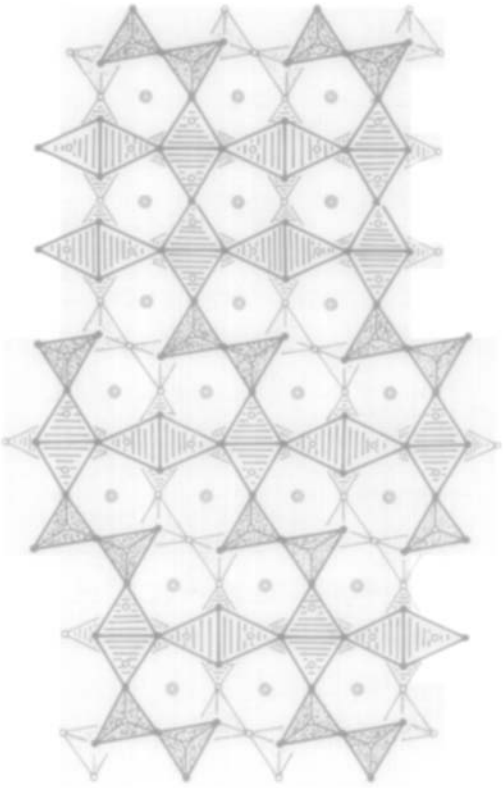

FIG. 7d. Intergrowth μ-Zr_4Al_3.

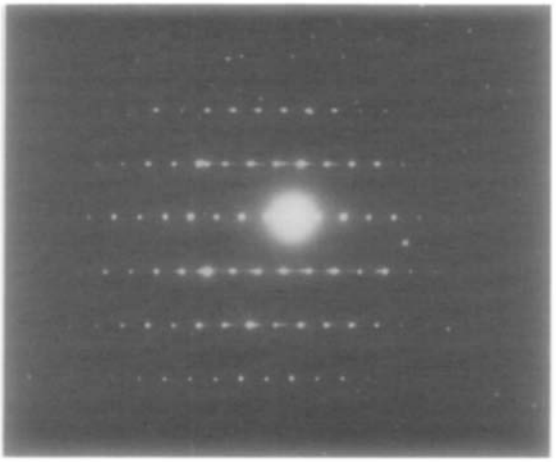

FIG. 8. Diffraction pattern of a typical μ-phase crystal. Electron beam parallel with [110].

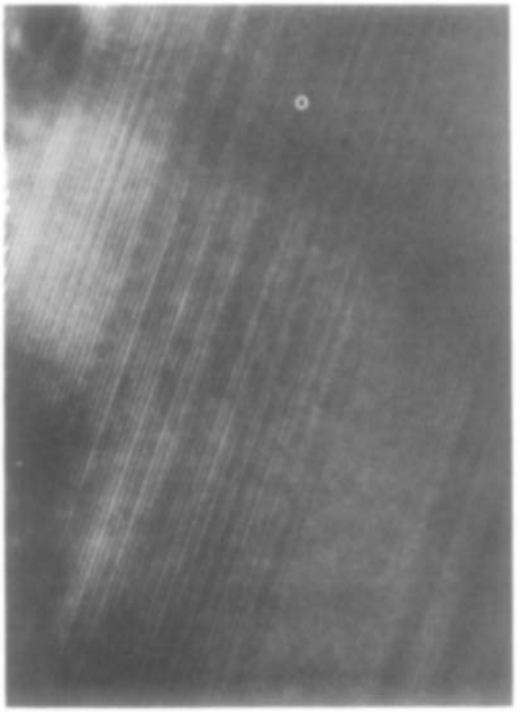

FIG. 9. The structure image of the same crystal as in Fig. 8. Fringes 8.6 Å apart.

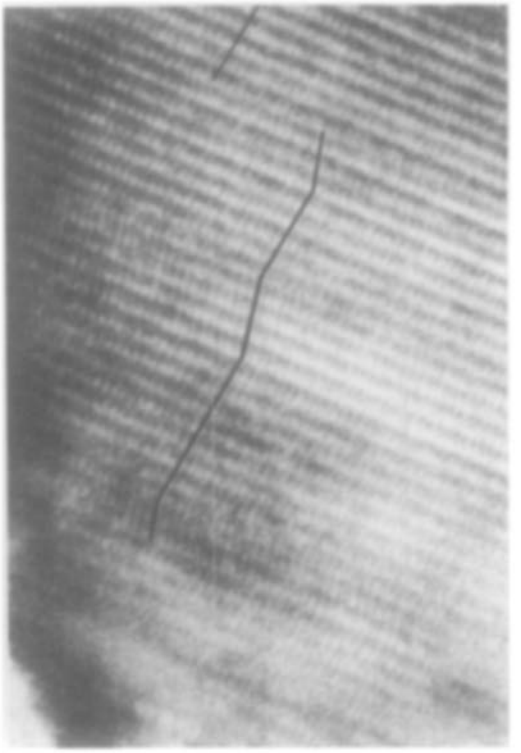

FIG. 10. Small region of the same crystal as in Fig. 9. pattern, reinforced by heavy ink lines. Planar contrasts are here resolved to a zigzag.

an underfocus of 900 Å is shown in Fig. 15. This calculated image agrees well with the observations in Figs. 12 and 13. In general, the calculated images of these types of structures change rapidly with focus variations, and this was also observed experimentally in the microscope.

Another kind of well-resolved planar defects in a crystal of the μ-phase is shown in Fig. 16. The small white dots form squares of an edge of approximately 4 Å. Two possible explanations are obvious, one is an intergrowth with a structure of the Zr_4Al_3 type, which we regard as very plausible, and the other is an intergrowth with a structure of $MgZn_2$ type (Figs. 7c, d). No image calculations were made, the need for better resolution or more suitable samples is obvious.

The *P*-Phase

Extensive disorder of intergrowth and twin type was frequently observed in crystals of the *P*-phase. Two dimensional images, of promising details, were easily observed, and this will be reported in a forthcoming article.

Conclusions

A sample of a Fe–Mo alloy, quenched from the melt, giving a diffuse X-ray powder pattern has been shown to consist of crystals of various phases. Most crystals were rich in planar defects, which explains the diffuse character of the powder pattern. Much more work needs to be done to develop techniques for the characterization of powder on atomic resolution. Properties in general and the effect of heat and mechanical treatment

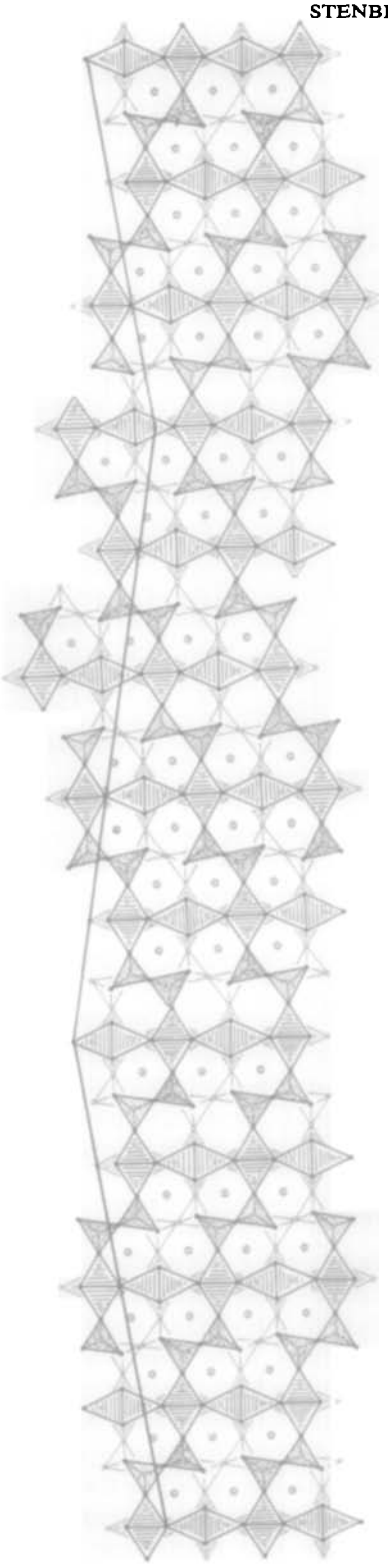

FIG. 11. Atomic structure for the zigzag region of Fig. 10.

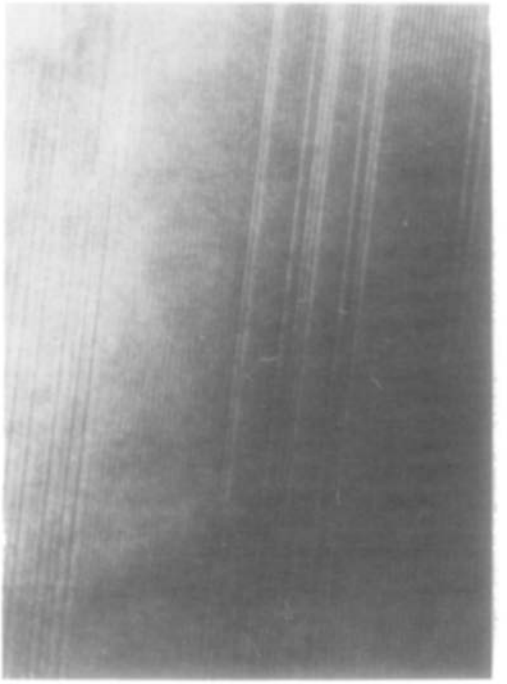

FIG. 12. Planar defects in the μ-phase.

should be correlated with the defect structure of powder crystals. Fundamentally it is now clear that the formation of planar defects in these alloy systems is structurally dependent as was proposed in Ref. *1*, and consequently intimately associated with the crystal growth mechanism. The complete absence of dislocations is interesting. Obviously the complex structures of these brittle materials offer alternative and simpler defects.

Acknowledgment

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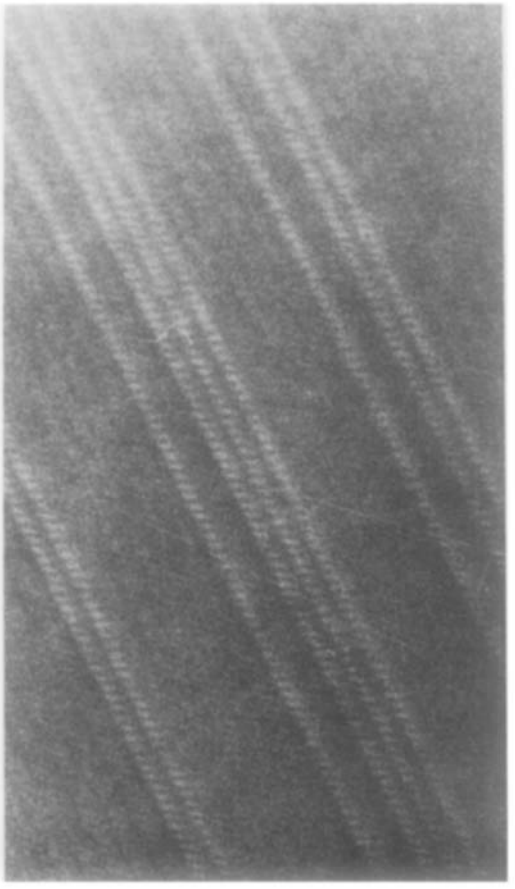

FIG. 13. Small region of crystal from Fig. 12 magnified.

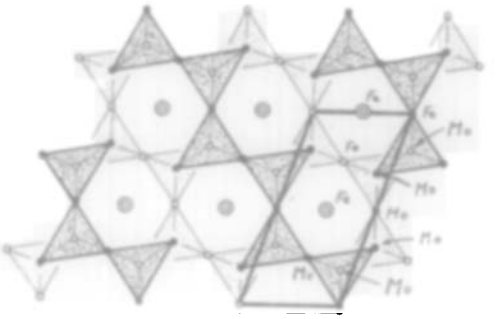

FIG. 14. Fe–Mo ordering indicated in an oblique unit of a Fe–Mo structure of Cu_2Mg type.

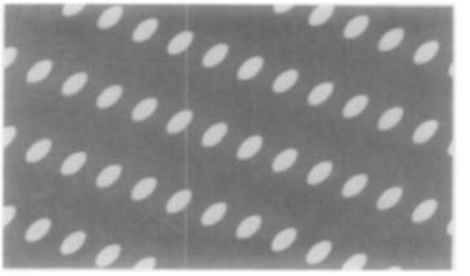

FIG. 15. Calculated image for a Fe–Mo structure of Cu_2Mg type.

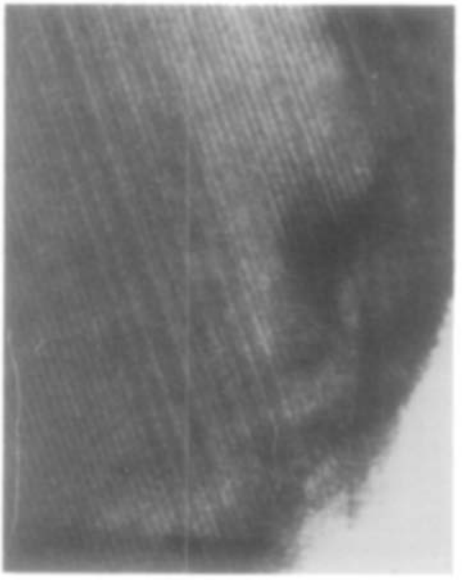

FIG. 16. Planar defects in a crystal of the μ-phase. Note small squares of white dots, approximately 4 Å apart. Fringe spacing 8.6 Å.

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