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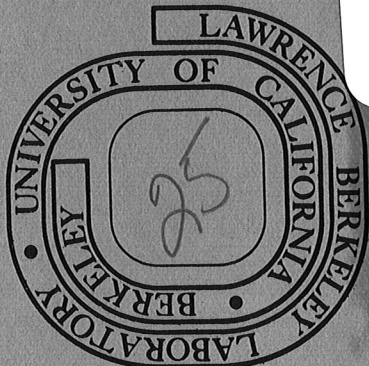
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ON THE MECHANISM OF MARTENSITE TRANSFORMATION
IN NEAR EQUIATOMIC NiTi ALLOY

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The martensitic-transformation in polycrystalline Ti-50.3 at pct. Ni alloy has been investigated using the technique of transmission-electron microscopy and diffraction. It was found that the extra reflections observed in the high temperature phase (CsCl, B2 type structure) are not related to the martensitic-transformation but are most likely associated with very fine ordered particles (less than 100Å) of a Ni-rich phase, which is coherent with the CsCl-structure. The streaming or shimmering effects observed in bright-field images of a number of alloys which undergo martensitic-transformation and have sometimes been interpreted as a manifestation of lattice oscillations, were not observed in the present investigation. The martensitic-transformation may occur by $\{110\}\langle 110\rangle$ inhomogeneous shear of the CsCl-structure.

I. Introduction

The thermoelastic martensitic-transformation in near equiatomic NiTi alloys has been the subject of a number of papers.¹⁻¹⁰ Several investigators noted in electron diffraction^{2,3,5,11-15} and X-ray precision patterns^{9,12} the existence of extra reflections at $1/3\{110\}$ reciprocal-lattice vectors of the high temperature phase (CsCl, B2-type structure). Chandra and Purdy¹¹ and Sandrock et al¹² attributed these extra reflections

to high amplitude vibrational modes arising from incipient lattice instability prior to the martensitic-transformation. Tong and Wayman¹⁶ have reported the observation of streaming or shimmering effects in bright-field images of the high temperature phase of a number of alloys (all of which undergo martensitic-type transformation) when cooled to a temperature approaching the critical temperature for the transformation. According to Tong and Wayman, these streaming or shimmering effects might also be expected in the case of NiTi. However, Tong and Wayman's observations have been attributed by Estrin et al¹⁷ to some artifacts. Since these pre-transformation effects are important in understanding the mechanism of martensitic-transformations, the present investigation has been undertaken to study the pre-transformation effects and to clarify the origin of the extra reflections.

II. Experimental Procedure:

All the specimens (sheets 1mm thick) were solution treated at 1000°C for 24 hrs. in quartz capsules under argon atmosphere, about 10^{-6} torr, and then quenched in ice water. Chemical analysis done after such treatment showed that:

Ni	55.4 wt. pct. (50.3 at. pct)
O	about 350 ppm
N	less than 10 ppm

The M_s temperature (temperature at which martensite transformation starts during cooling) as determined from the peak of the electrical resistivity vs. temperature diagram¹² was found to be about 55°C. At room temperature, the material was partially transformed into martensite as determined from X-ray diffractometer traces.

Thin foils for transmission microscopy were prepared from the heat treated sheets by first thinning down to about 0.08 mm in a solution of 1 HF: 9HNO₃ by volume. Discs 2.3 and 3 mm diameter were spark eroded from the thinned sheets and then electrolytically polished by a jet polishing technique in a solution of 1HNO₃:3Methanol by volume. The specimens were examined in a Siemens IA EM and a Philips 100 EM equipped with cooling and heating stages. All the observations were made at an operating voltage of 100kV. In order to observe the formation of martensite inside the microscope, foils were first heated until all the existing martensite disappeared at about 375°C and then cooled inside the microscope. The accuracy of temperature measurement was better than ±1°C.

III Experimental Results and Discussion:

A. Pre-transformation Effects:

Figure 1 shows a series of bright-field images and their corresponding selected-area electron diffraction patterns taken during cooling from room temperature. The initial orientation was (111)_{B2}. It was observed that during cooling no significant change occurred until the temperature reached about -30°C. At about -30°C, diffuse streaks can be seen along {110}_{B2} reciprocal-lattice vectors with a tendency toward splitting of the diffraction maxima, (Figure 1b). This signifies a deviation from cubic symmetry. Similar effects have also been noted in X-ray diffractometer traces of 51.3 at pct. Ni alloy.¹⁸ Signs of buckling and straining of the foil can be seen in the corresponding image. This is evident from the distortion of the bend contour, although no definite martensite crystals could be detected at this stage. A similar observation has also been reported for splat-cooled Au-47.5 at pct. Cd alloy.¹⁹

At -40°C , fine parallel bands appeared as shown in Figure 1c. This temperature (-40°C) was thus taken to be the M_s temperature in the foil. These parallel bands were further developed upon further cooling (Fig. 1d). These bands were either twin-related domains within a martensite-variant or different variants of martensite. The appearance of these bands was accompanied by the disappearance of the diffuse streaks and the complete splitting of the diffraction maxima (Fig. 1c). The streaming effect observed by Tong and Wayman¹⁶ was not observed in the present case.

The martensite structure of the particular alloy investigated was found to be a two-layer close packed structure (2H-structure according to the notations of Sato et al.²⁰) with a nearly orthorhombic unit cell slightly distorted to monoclinic. The basal plane of the martensite structure is derived from a $\{110\}_{B2}$ plane. Figure 2 shows the correspondence between the predicted and observed diffraction patterns of the martensite basal plane (001) assuming that this is derived from a $\{110\}_{B2}$ plane. Figure 3 shows a projection of a $\{110\}_{B2}$ plane. This was assumed to represent the base of an orthorhombic unit cell according to Sato et al.²⁰ The relative intensity distribution in reciprocal space of the predicted pattern of Figure 2 was calculated from:

$$|F|^2 = [f_{\text{Ni}} + f_{\text{Ti}} \exp 2\pi i(h/2 + k/2)]^2$$

It is to be noted that, if the superlattice spots of the observed pattern of Figure 2 are ignored, the main spots form a hexagonal array. This suggests that during the transformation a $\{110\}_{B2}$ plane transforms into a closer-packed plane. This is in agreement with the mechanism proposed by Nishiyama and Kajiwara²¹ for body centered cubic (ordered CsCl or

Fe₃Al structures) to close-packed structure transformations.

It is to be noted that {110}<110> shear can provide the right shear strain to transform a {110}_{B2} plane into a closer-packed plane as shown schematically in Fig. 4. Cohen et al.²² have proposed a dislocation formalism for bcc → close-packed structure transformations which involve dissociation of a/2<111> dislocation on {110} plane according to:

$$a/2[111] \rightarrow a/8[011] + a/4[211] + a/8[011]$$

In the present case, since the martensite has a 2H-structure (ABAB...) and that the {110}_{B2} planes have already the proper stacking sequence as shown in Fig. 5, the structural change can be achieved by {110}<110> inhomogeneous shear on every other {110} plane in addition to some homogeneous Bain strain. Since the structure is ordered, extension of a/8<011> partials would be dependent on the energy of the anti-phase boundary (APB) created as well as the stacking fault. The available evidence points out that NiTi may be ordered up to its melting point.²³⁻²⁶ The energy σ of APB on a {110} plane was estimated from the expression^{27,28}:

$$\sigma = \frac{-4n^2 h \epsilon}{a^2 (h^2 + k^2 + 1)^{1/2}} \quad \text{for } h \geq k+1$$

where $\epsilon = \epsilon_{AB} - 1/2(\epsilon_{AA} + \epsilon_{BB}) = \frac{-KT_c}{4}$, n is unity for stoichiometric compounds, ϵ_{AB} is the energy of A-B bond, ϵ_{AA} that of A-A bond, ϵ_{BB} that of B-B bond, (hkl) are the indices of the APB plane, K is Boltzmann's constant, a is the lattice parameter (3.01Å^o for the alloy investigated as determined from X-ray diffractometer traces) and T_c was chosen to be the melting point. σ_{110} was found to be about 169 ergs/cm². The equilibrium width (w) between the two outer a/8<011> partials in screw orientation was estimated from:

$$w = \frac{Gb^2}{2\pi K\sigma}$$

G (the shear modulus) was estimated from Young's modulus determined from stress-strain data of the alloy investigated near the transformation temperature, b is the Burgers vector of $a/8\langle 011 \rangle$ partial and K was taken as unity. The equilibrium separation w estimated in this way was found to be only about $0.2\overset{\circ}{\text{A}}$ which is 0.08 of the interatomic distance. Therefore $a/8\langle 011 \rangle$ partials can not be considered to exist in the classical sense. The structural change can be considered to occur by inhomogeneous shear "shuffles" on every other $\{110\}_{B_2}$ plane along $\langle 110 \rangle_{B_2}$ directions in addition to some homogeneous Bain strain as described by Lieberman for the case of Au-Cd.^{29,30} The nucleation of the transformation shear would be expected to be easier at a dislocation, although dissociation of a perfect dislocation in the classical sense is highly unlikely.

The present results suggest that the transformation shear starts on a very fine scale before definite martensite crystals can be detected (Fig. 1) and are in agreement with Zener's suggestion³¹ that β -phase alloys (bcc structure in the disordered state) may become mechanically unstable toward $\{110\}\langle 110 \rangle$ shear during cooling and tend to transform martensitically to closer-packed structures. This has been verified in several β -phase alloys e.g. Au-Cd³², Cu-Zn, Au-Zn and Au-Zn³³, Au-Cu-Zn³⁴ by measuring the shear constant $1/2(C_{11} - C_{12})$ (this represents the resistance of the lattice to $\{110\}\langle 110 \rangle$ shear) as a function of temperature. This shear constant was found to reach a minima at the M_s temperature. Unfortunately no such measurements have

yet been done on NiTi due to the difficulty of preparing single crystals. However, the observed decrease in elastic moduli³⁵, yield strength³⁶ and hardness³⁷ as the M_s temperature is approached suggest that the CsCl-structure may be "softened" as the M_s temperature is approached.

B. Origin of the Extra Reflections

If the extra reflections observed in the high temperature phase were associated with pre-martensitic lattice waves, one would expect to observe these reflections in the vicinity of the M_s temperature. In the present case, the M_s temperature in thin foils was found to be about -40°C . Figure 6 shows a bright-field image and its corresponding selected-area diffraction pattern taken at 400°C . Very weak extra spots can be seen at $1/3\{110\}_{B_2}$. In the corresponding image, regions of dark contrast characteristic of elastic strain field can be seen. The observation of these extra reflections at that high temperature makes it difficult to imaging that these are related to the martensitic-transformation. Figure 7 shows the (110) and (111) diffraction patterns and their corresponding bright-field images taken at room temperature from partially transformed specimen. The extra spots at $1/3\{110\}_{B_2}$ in addition to extra spots at $1/2\{001\}$ can be seen. In the corresponding images regions of dark contrast similar to those observed at 400°C can be seen. Figure 8 shows a bright-field image of a martensite plate surrounded by retained high temperature phase and its corresponding diffraction pattern. Again, the extra spots at $1/3\{110\}_{B_2}$ and the associated dark contrast can be seen. These observations indicate that the extra spots are not destroyed by the martensitic-transformation. It is to be noted that NiTi is now known to have a very narrow homogeneity

range below about 500°C ²³⁻²⁶. Therefore, one would expect that in Ni-rich compositions which have been widely investigated, a second phase may form prior to the martensitic-transformation. The appearance of the extra reflections and the associated observed contrast suggest that this phase (expected to be Ni-rich) is ordered and highly coherent with the CsCl-structure. Individual particles could not be resolved in agreement with the observations of Gupta.¹⁵ Therefore it is suggested that the observed contrast is due to overlapped elastic coherency strain of very fine particles (less than 100\AA) i.e., net strain contrast as described by Thomas³⁸. Figure 9 shows a tentative atom arrangement in two dimensions which could account for the $1/3\{110\}$ and $1/2\{001\}$ extra reflections. The atom arrangement in the third dimension may remain the same as in the CsCl-structure and this explains the absence of the $1/3\{110\}$ apots in $\{110\}$ patterns as has been noted by Sandrock et al¹² and in the present investigation. Extra spots have also been observed in the high temperature phase of a number of alloys which undergo martensitic-transformation³⁹. Delaey et al³⁹ have attributed these spots in Ag-Cd to coherent precipitate particles. However, Nagasawa^{40,41} suggested that these are due to pre-martensitic lattice waves although they were observed at a temperature which is 100°C above the M_s . Nagasawa⁴¹ could not give an explanation for this observation. Therefore it seems likely that in Ag-Cd, the extra spots are due to coherent precipitate particles as is evident from the results of Delaey et al⁴³.

IV Conclusions

(1) The martensitic-transformation in Ti-50.3 at pct. Ni alloy occurs by inhomogeneous $\{110\}\langle 110\rangle$ shear of the CsCl-structure in addition to some homogeneous Bain strain. This shear is not associated with partial dislocations due to high energy anti-phase boundary.

(2) Streaming or shimmering effects in bright-field images that have sometimes been interpreted as a manifestation of lattice oscillations were not observed in this investigation.

(3) Extra reflections from the high temperature phase at $1/3\{110\}$ and $1/2\{001\}$ were observed at a temperature far above the M_s . Therefore these are not related to the martensitic-transformation.

ACKNOWLEDGEMENTS

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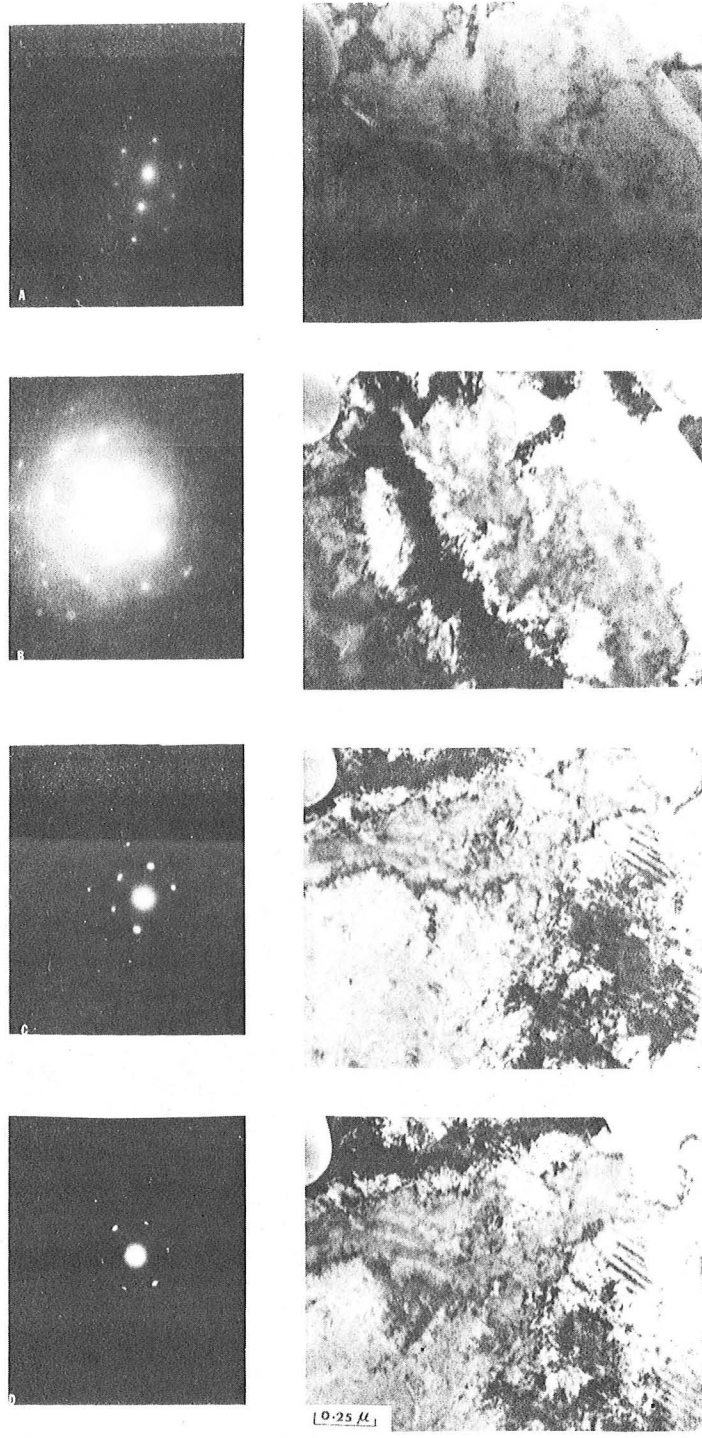
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Figure Captions

- Figure 1. Example of a cold-stage electron microscopy experiment showing the formation of martensite (bright-field images and their corresponding diffraction patterns). (a) room temperature, (b) -30°C , (c) -40°C , (d) -100°C .
- Figure 2. Electron-diffraction pattern corresponding to the basal plane of martensite (a) Predicted (b) Observed.
- Figure 3. Schematic illustration in two dimensions showing transformation of a $\{110\}_{\text{B}_2}$ plane into the basal plane of martensite.
- Figure 4. Projection of $\{110\}_{\text{B}_2}$ plane showing the effect of $\{110\}\langle 110\rangle$ shear.
- Figure 5. Stacking sequence of $\{110\}_{\text{B}_2}$ planes. (a) face-centered tetragonal cell delineated within four CsCl-cells. (b) the face-centered tetragonal cell viewed as an alternate stacking of $\{110\}_{\text{B}_2}$ planes.
- Figure 6. Microstructure of the high temperature phase at 400°C . (a) $(111)_{\text{B}_2}$ selected-area diffraction pattern showing weak extra spots at $1/3\{110\}_{\text{B}_2}$. (b) Bright-field image showing elastic strain contrast.
- Figure 7. Microstructure of the high temperature phase at room temperature. (a) $(110)_{\text{B}_2}$ pattern showing extra spots at $1/2(001)_{\text{B}_2}$ and the corresponding bright-field image. (b) $(111)_{\text{B}_2}$ pattern showing extra spots at $1/3\{110\}_{\text{B}_2}$ and the corresponding bright-field image.

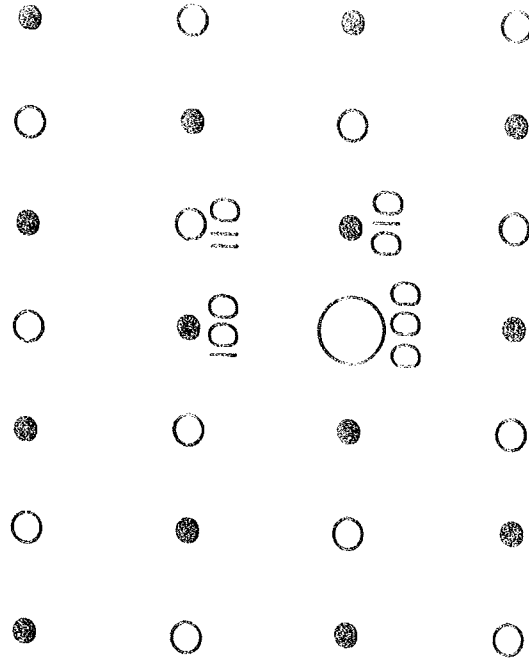
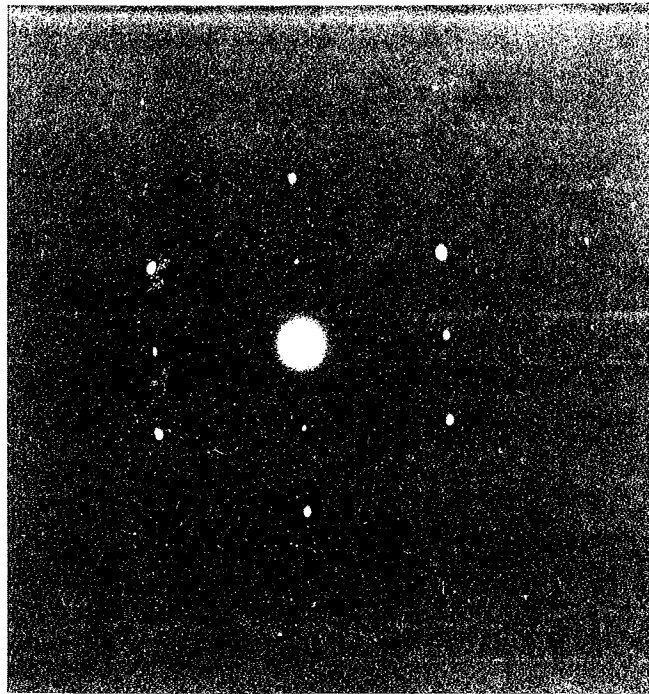
Figure 8. (a) $(111)_{B2}$ selected-area diffraction pattern taken from a region of (b) containing both martensite and retained CsCl-structure and showing extra spots at $1/3\{110\}_{B2}$.
(b) Bright-field image at room temperature showing a martensite plate surrounded by retained CsCl-structure, the dark contrast in the retained CsCl-structure is typical of elastic-strain contrast.

Figure 9. Tentative atom arrangement in two-dimensions which could account for the extra spots at $1/3\{110\}_{B2}$ and $1/2\{001\}_{B2}$.



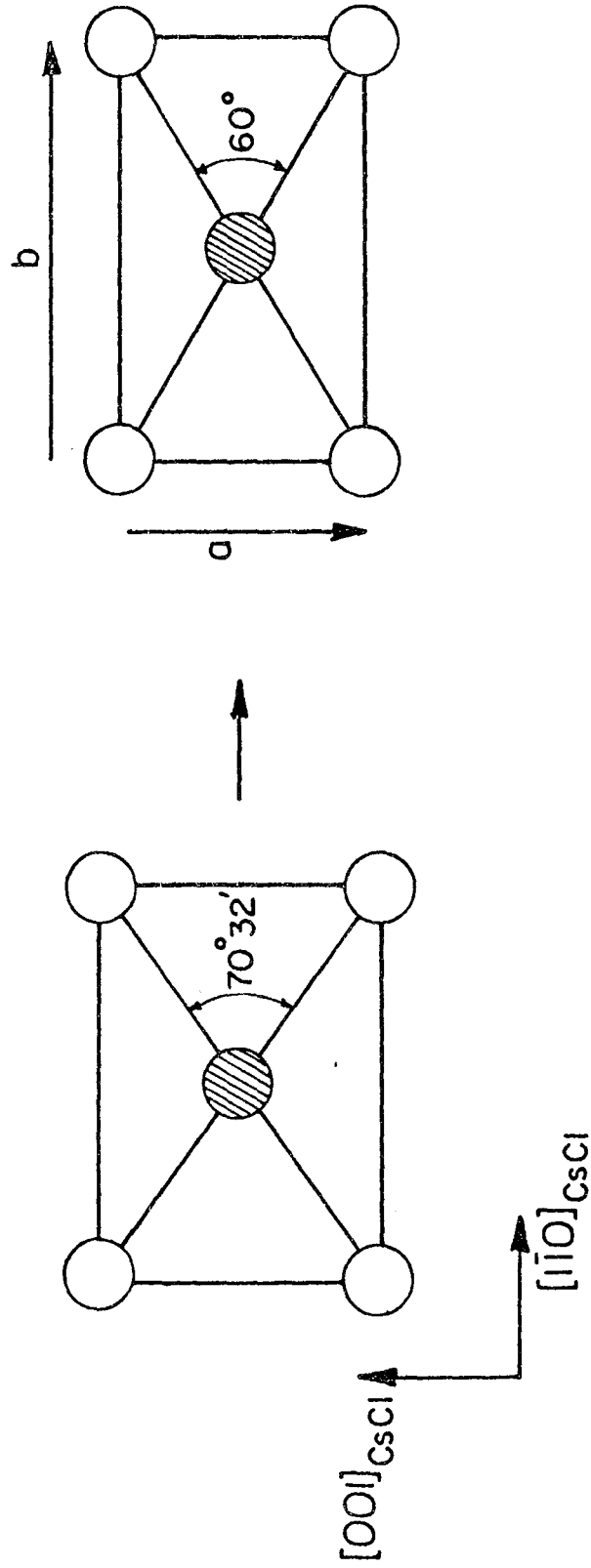
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Fig. 1



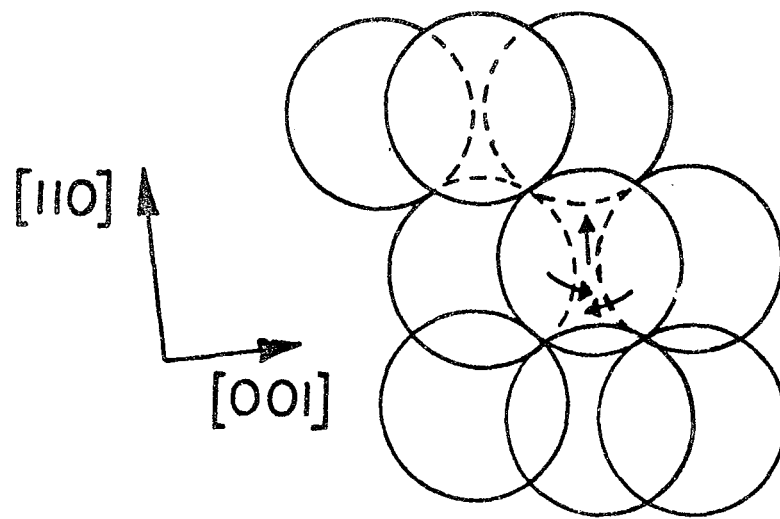
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Fig. 2



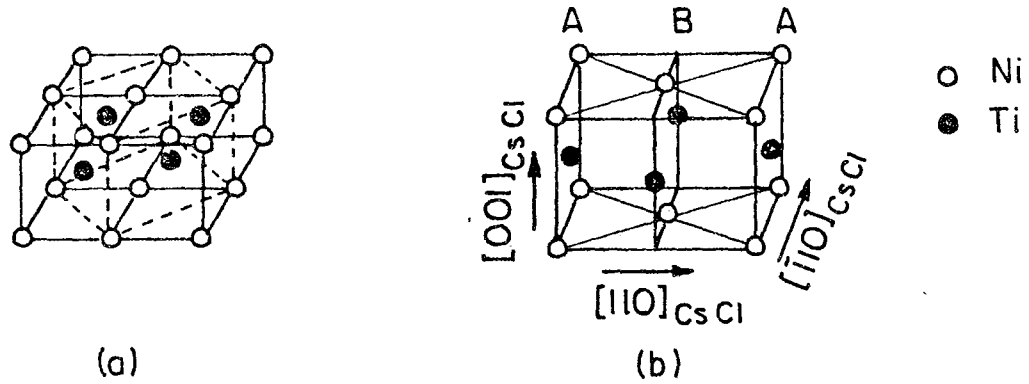
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Fig. 3



XBL 764-6759

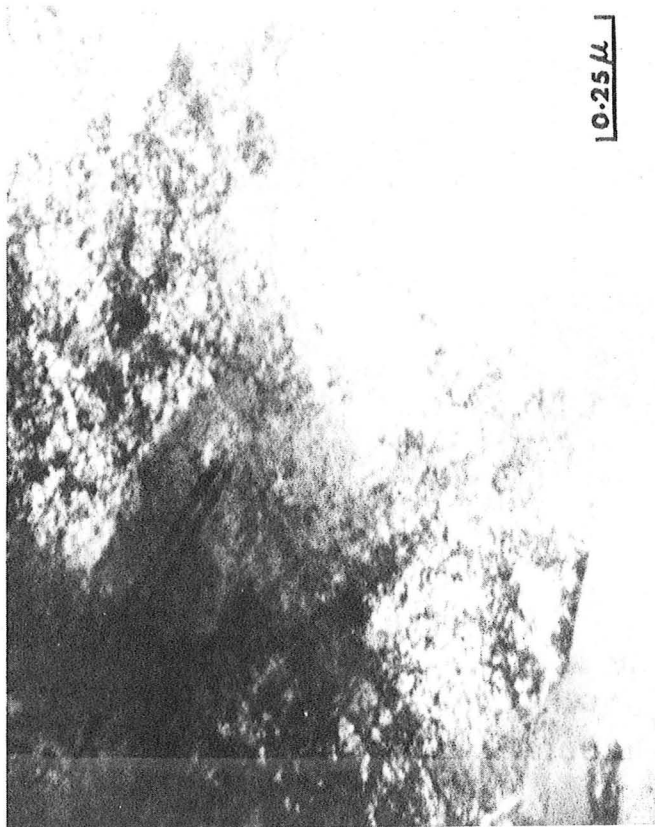
Fig. 4



- (a) A face-centered tetragonal cell (dotted lines) delineated within four CsCl cells.
- b The CsCl structure viewed as alternate stacking of $\{110\}$ planes.

XBL 752-5868

Fig. 5



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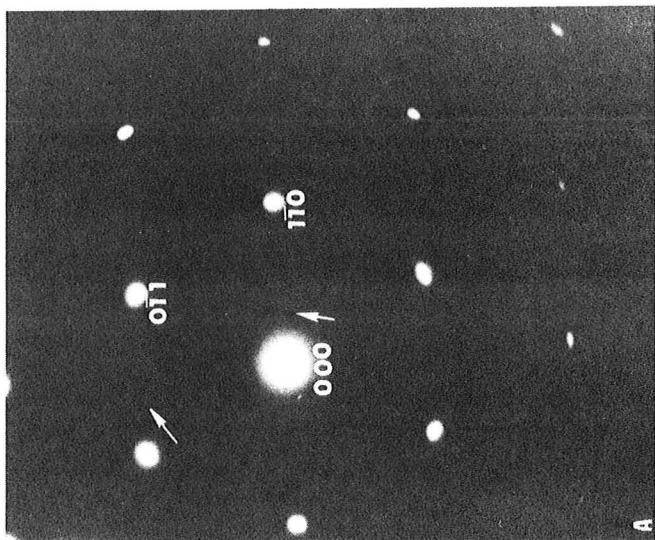
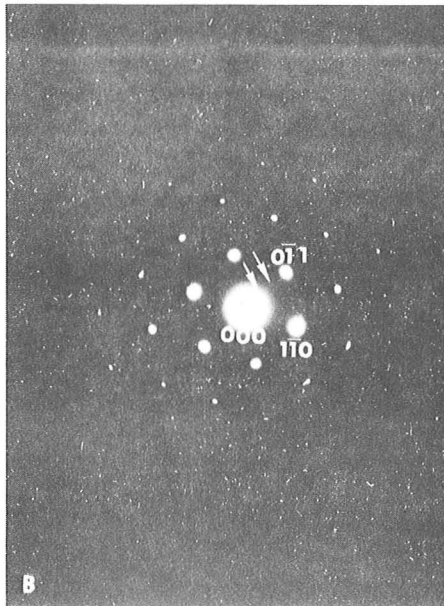
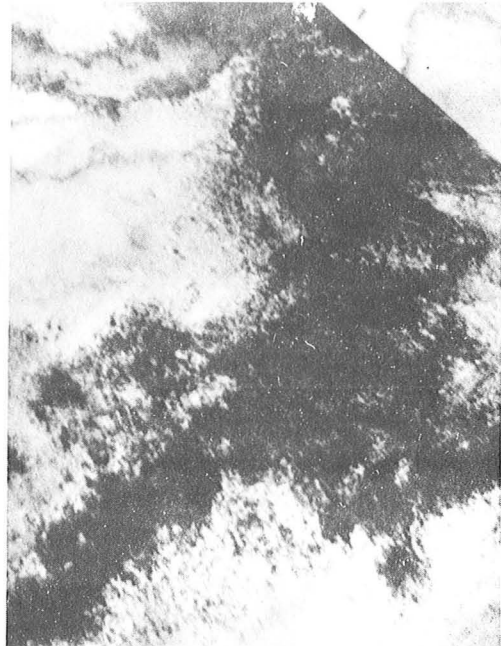
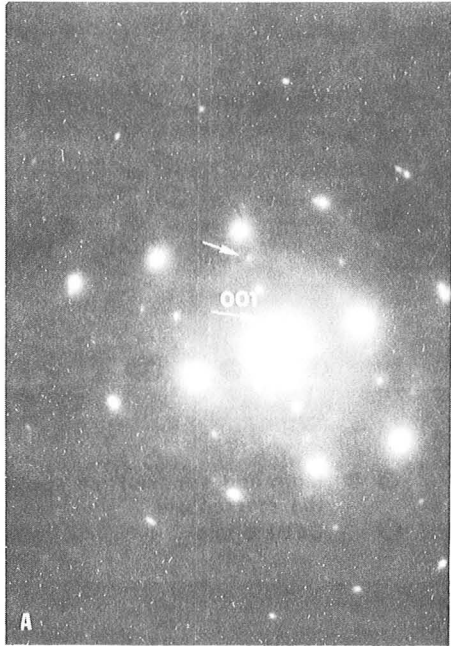
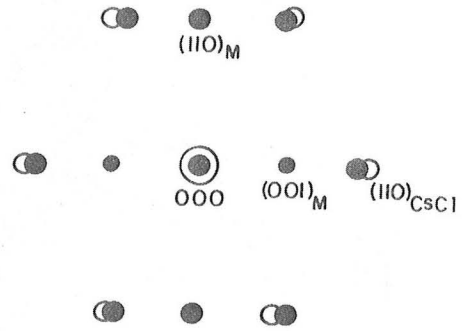
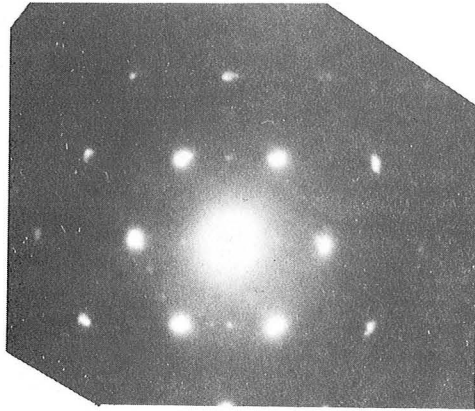


Fig. 6

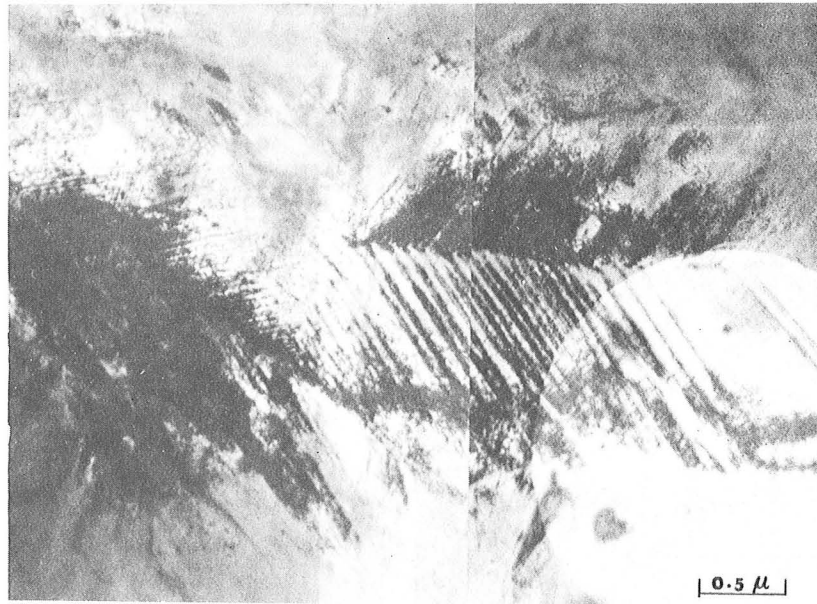


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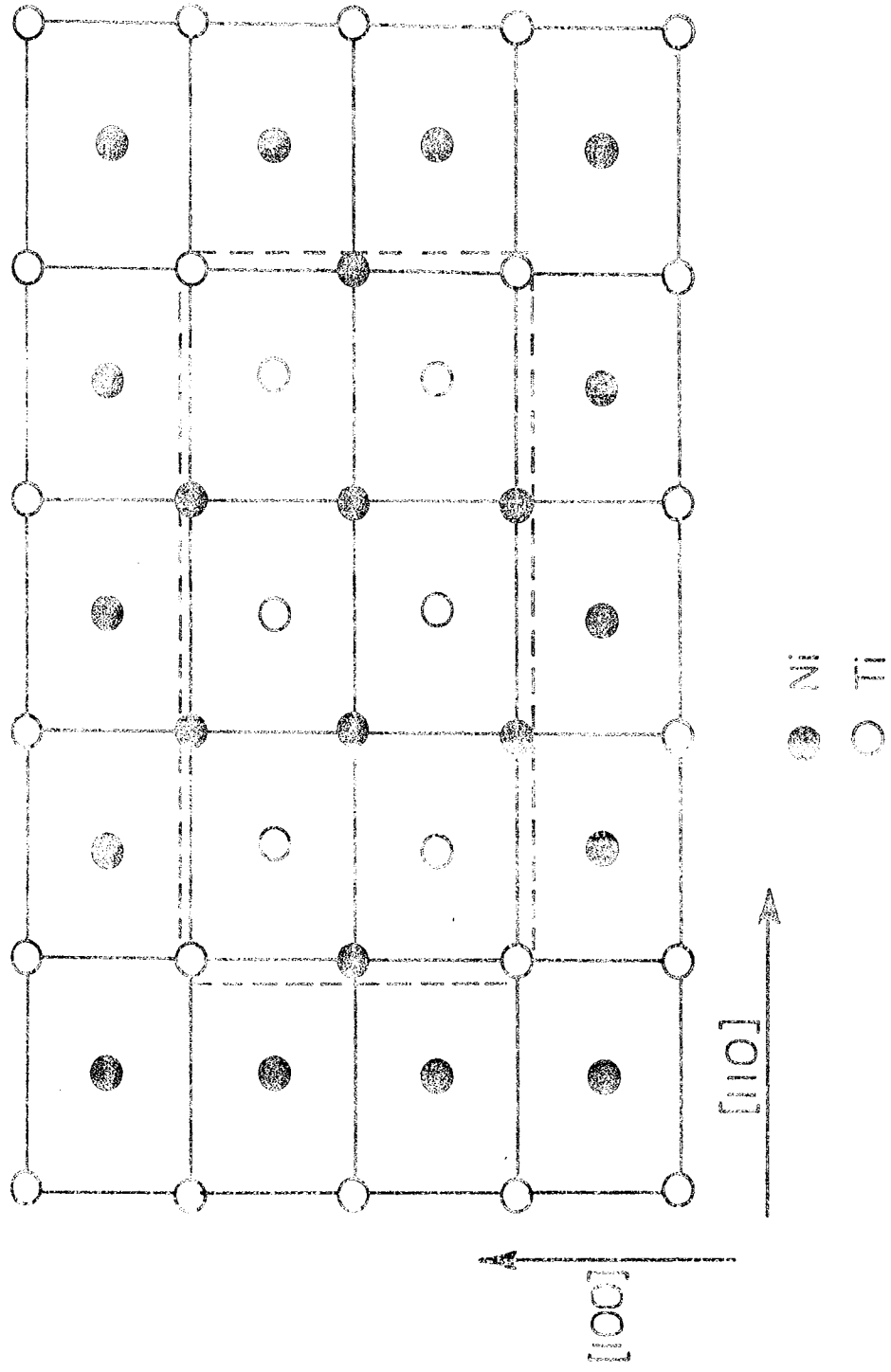
Fig. 7



- ● Main and superlattice spots of the martensite
- CsCl spots



XBB 765-3863



XBL 764-6770

Fig. 9

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