OVERVIEW

Recent Studies on the Precise Crystal-Structural Analyses of Martensitic Transformations

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Recent studies on the martensitic transformations by precise crystal-structural analyses have been reviewed. Crystal structures of the B19' and ζ_2' martensites in Ti-Ni and Au-Cd alloys, respectively, which had been controversial for a long time because of their complexity, and the γ_1' and γ_2' martensites in Cu-Al-Ni and Au-Cd alloys, respectively, have been unambiguously identified in a straightforward manner by the single crystal four-circle X-ray diffraction method. Moreover, by means of a newly developed structural analysis called ALCHEMI, the site occupancies of Ni atoms in Cu-Al-Ni alloys, Cu and Zn atoms in Cu-Au-Zn and Cu-Zn-Al alloys and various third X elements in Ti-Ni-X alloys have uniquely been determined, which are generally difficult to be determined by conventional X-ray and electron diffraction because of the similarity in atomic scattering factors of the atoms involved or of their small amounts contained. On the other hand, a new intermediate phase was found in a very narrow temperature range above M_s temperature for the fcc to fct transformation in Fe-Pd alloys owing to an accurate temperature control. Interesting phenomena were also found in some alloys such as Ti-Ni-Fe, Ni-Al, Fe-Pt and Cu-Fe through extensive and precise structural analyses. The exact crystallographic data obtained for these martensites will be indispensable to elucidate the origins and the mechanisms of the respective martensitic transformations. Precise crystal-structural analyses for some shape memory alloys were shown to serve for understanding the origins of the aging effects in the alloys.

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I. Introduction

In the 1930's epoch-making discoveries were made in the field of studies on the martensitic transformation:

Kurdjumov and Sachs⁽¹⁾ found that there exists a definite orientation relationship between the martensite and austenite lattices in an Fe-1.4mass% C steel, while Nishiyama⁽²⁾ observed another one between them in an Fe-30.0%Ni alloy. Based on these experimental findings early shear mechanisms for the martensitic transformations were put forward. Although the shear mechanisms were too simple to be consistent with the experimental facts accumulated later on, and denied eventually⁽³⁾, the above orientation relationships are now widely known as the Kurdjumov-Sachs (K-S) and the Nishiyama (N) relationships, respectively, in the celebration of their pioneer works. Early investigations on the martensitic transformations were thus rather limited to ferrous alloys. However, the martensitic transformations were afterwards found successively to occur in nonferrous alloys such as noble metal based β phase alloys, and furthermore in some ceramics⁽⁴⁾⁻⁽⁶⁾.

The martensitic transformation is now well-defined to be the diffusionless first order phase transition. The nucleation and growth, the crystallography, the ther-

modynamics and kinetics, and the mechanical properties associated with the transformation such as the shape memory effects, pseudoelasticity and so on have been extensively studied so far⁽³⁾⁻⁽¹³⁾, and useful pieces of knowledge as to them have been accumulated. Nevertheless the origins and the mechanisms of the martensitic transformations are not clear yet. For the further understanding of the martensitic transformations, it is essential to know crystal structures of martensite phases as precisely as possible, and parent phases as well. In respect of this, remarkable development has been achieved for these several years owing to the progress in monocrystallizing technique not only of parent phase but also of martensite, which enables us to utilize precise single crystal X-ray and neutron diffraction methods, and to the development of a new crystal-structural analysis method called ALCHEMI utilizing electron channeling effects in crystals (described later). In this article, extensive studies recently made from a viewpoint of precise crystal-structural analysis on the martensitic transformations are reviewed. Refinements of crystal structures of various martensites widely known and findings of new martensites are described in the section II, and site occupancies of atoms in parent lattices of some noble metal-based β phase and Ti-Ni based ternary alloys are in section III. Such studies are believed to eventually serve for making clear the origins and the mechanisms of the respective martensitic transformations from a microscopic point of view. Precise crystal-

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structural analyses of martensites and parent phases in some shape memory alloys are shown to be useful for understanding the origins of the aging effects in them, such as changes of the forward and reverse transformation temperatures⁽¹¹⁾. Crystal-structural studies reported by the early 1980's have been reviewed elsewhere⁽¹⁴⁾⁽¹⁵⁾.

II. Refined Crystal Structures of Martensites

1. Ti-Ni alloys near equiatomic composition

(1) B19' martensite

The Ti-Ni alloys near equiatomic composition are widely known as the most excellent shape memory alloy among those found so far, but crystal structure of the martensite closely related with the effects had been controversial for a long time⁽¹⁵⁾. One reason for this was that single crystal diffraction methods were not available for precise crystal-structural analysis because single crystals of the alloys were very difficult in obtaining in the martensite phase. Kudoh *et al.*⁽¹⁶⁾, however, eventually succeeded in producing single crystals of a Ti-49.2 at.%Ni alloy by strain anneal method and making single crystals of the martensite by stress-induced transformation technique. Single crystal precession photographs of X-ray diffraction unambiguously showed the crystal structure to be monoclinic and the space group to be $P2_1/m$. By using a four-circle X-ray diffractometer they determined the lattice parameters to be $a=0.2898$, $b=0.4108$, $c=0.4646$ nm, and $\beta=97.78^\circ$, which are essentially the same as those previously reported by several workers⁽¹⁷⁾⁽¹⁹⁾, and the atomic parameters to be those in Table 1, where those determined by Michal and Sinclair⁽¹⁹⁾ are also shown. The latter data were adopted as the initial values for the least-squares refinement, where 307 independent observed reflections were used, carefully excluding those affected by very small amounts of (111) twins⁽¹⁸⁾. The atomic parameters as to four atoms in the monoclinic unit cell were refined to 4.5% of the R-factor (5.7% of the weighted R-factor), while those by Michal and Sinclair resulted in $R=38.6\%$ (40.1% in wR). The crystal structure identified in a straightforward manner is schematically shown in Fig. 1. Since the values of R-factors are very small, the crystal structure thus derived is conceivable to be an ultimate one. As seen in the figure, the crystal structure is largely different from the ordinary long period stacking order structures of martensites in noble metal-based β phase alloys with respect to shuffling of atoms⁽³⁾: While the latter is regarded as two-

Fig. 1 Crystal structure of the B19' martensite in a Ti-Ni alloy identified by Kudoh *et al.*⁽¹⁶⁾, viewed from the [010] direction.

dimensional close-packing of basal plane, the former is a three-dimensionally close-packed one. Thus the origin of the streaks along the c^* direction in electron diffraction observed previously by Otsuka *et al.*⁽¹⁸⁾ is not obvious in the crystal structure shown in Fig. 1. Kudoh *et al.*⁽¹⁶⁾ rationalized the streaks by the presence of faults on the (001) plane in terms of the partial pseudo-mirror existing in the structure.

Complicated atomic shuffles have also been suggested by the present authors to take place in another monoclinic martensites of Ti-Ni-X ($X=\text{Cu}^{(20)}$, $\text{Fe}^{(21)}$) alloys. The monoclinic martensite in Ti-Ni-Fe alloys was observed to be formed in thin foil specimens, but that in Ti-Ni-Cu alloys was in bulk specimens. As far as the Bain distortion is concerned, the transformations in these alloys are not so different from each another. But the atomic shuffles involved are entirely different and the unit cells become largely different in size from each another thereby. These facts implies that there exists a certain microscopic origin determining crystal structure of martensite. The origin seems to be closely related to the mechanism of the martensitic transformations and remains to be clarified.

Crystal structure of the B19' martensite was recently re-examined in polycrystalline state by means of time-of-flight neutron diffraction techniques, and the result reported⁽²²⁾ was inconsistent with the above one. Since the alloy examined was Ni-rich and was heat-treated at 823 K for 2.5 h, therefore, there might be a possibility that the B2 to R phase transformation (discussed later) had taken place due to the precipitation of Ti_3Ni_4 ⁽²³⁾⁻⁽²⁵⁾ during the heat treatment. The Bragg peak spectra obtained by the neutron diffraction should thus be carefully analyzed, taking account of the possibility and also the well-refined crystal structure mentioned above.

(2) R phase

It is well recognized in binary Ti-Ni and some ternary Ti-Ni-X alloys under certain conditions upon cooling that another phase with a rhombohedrally distorted lat-

Table 1 Atomic parameters for the B19' martensite in a Ti-Ni alloy by Kudoh *et al.*⁽¹⁶⁾, together with those by Michal and Sinclair⁽¹⁹⁾ for comparison.

Structure	Kudoh <i>et al.</i>			Michal and Sinclair		
Ti	0,	0,	0	0,	0,	0
	0.1648,	1/2,	0.5672	0.055,	1/2,	0.558
Ni	0.6196,	0,	0.4588	0.580,	0,	0.472
	0.5452,	1/2,	0.1084	0.475,	1/2,	0.086

tice of the B2 parent one appears preceding the formation of the B19' martensite. This phase, usually called the R phase, is paid a good deal of attention in connection with the practical application of these shape memory alloys. Nevertheless the exact crystal structure of the R phase including the atomic parameters has not been made clear yet, although it is coming into light gradually. Goo and Sinclair⁽²⁶⁾ examined it in a Ti-47Ni-3Fe (at.%) alloy through selected area and convergent beam electron diffraction techniques. Formation temperature of the R phase in this alloy is well separated from that of the B19' martensite⁽²⁷⁾ and hence this alloy is suitable for a close examination of the R phase without interference of the B19' martensite, as actually done by Hwang *et al.*⁽²⁸⁾ According to Goo and Sinclair, reciprocal lattice of the R phase was a primitive hexagonal one and the space group was $P\bar{3}1m$. Wu and Wayman⁽²⁹⁾ constructed the three dimensional reciprocal lattice of the R phase formed in an aged Ti-51 at.%Ni alloy from its electron diffraction patterns, paying attention to the existence of the $\{110\}_{B2}$ and $\{100\}_{B2}$ twins in the R phase⁽³⁰⁾, and they proposed tentative atomic shuffles involved in the B2 to R transformation. It appears, however, that the uniformly distorted B2 parent lattice along its $\langle 111 \rangle$ direction cannot bring about the so-called $1/3$ reflections at all. Thus, a thorough investigation is needed for the structural analysis by such a straightforward method as the single crystal X-ray or neutron diffraction method.

(3) "Incommensurate phase"

Salamon *et al.*⁽³¹⁾ first reported through a neutron diffraction study on a Ti-46.8Ni-3.2Fe (at.%) alloy that the so-called $1/3$ reflections arising in electron, X-ray or neutron diffraction above the formation temperature of the R phase in Ti-Ni based alloys are incommensurate before they lock into the exact commensurate value of

$1/3$ at lower temperature. A high resolution X-ray diffraction study by Shapiro *et al.*⁽³²⁾ revealed that not only the satellites are incommensurate as to their positions, but also the incommensurate wave vector and the width of the satellites vary from Brillouin zone to Brillouin zone. Figure 2(a) shows a schematic representation of the observed variation of satellites in the (001) reciprocal lattice plane of the B2 parent phase, which was obtained from a Ti-46.8Ni-3.2Fe (at.%) alloy single crystal at 226 K, where the incommensurate satellites appeared at 232 K and the B2 to R transformation took place at 224 K. Such a feature as shown in Fig. 2(a) is inconsistent with the ordinary incommensurate structure with charge-density waves or lattice-displacement waves. Salamon *et al.*⁽³³⁾ pointed out that such an anomalous incommensurability is systematically reproducible if only the satellites are assumed to be shifted to the positions expected in the R phase, while the main Bragg peaks still maintain the original cubic positions. This peculiar reciprocal lattice called the ghost lattice is schematically shown in Fig. 2(b). Similar incommensurability of satellites was also observed⁽³⁴⁾ in X-ray diffraction arising from a Au-50 at.%Cd alloy single crystal at only about 3 K above M_s temperature for the B2 to ζ_2 transformation (described later). Theoretical interpretations of the ghost lattice have been attempted in terms of modulated lattice relaxation or embryonic fluctuation⁽³⁵⁾⁽³⁶⁾ and coupling of sinusoidal modulations to lattice strain⁽³⁷⁾. From an experimental standpoint, however, it seems that further studies are necessary to check the existence of some defects corresponding to the theoretically proposed ghost lattice by means of some direct methods, such as high resolution electron microscopy.

Fig. 2 (a) Schematic representation of the shift pattern of satellites in the (001) reciprocal lattice plane observed by Shapiro *et al.*⁽³²⁾ in a Ti-Ni-Fe alloy. (b) Schematic representation of the ghost lattice proposed by Salamon *et al.*⁽³³⁾ (delineated by dashed lines).

2. β phase alloys

(1) ζ'_2 martensite in near equiatomic Au–Cd alloys

Very recently Ohba *et al.*⁽³⁸⁾ eventually succeeded in solving a long-standing question as to crystal structure of the ζ'_2 martensite in near equiatomic Au–Cd alloys. Since the discovery of the ζ'_2 martensite by Köster and Schneider⁽³⁹⁾ in 1940, its crystal structure had been considered to be complicated and hence remained unclear for a long time⁽⁴⁰⁾. Vatanayon and Hehemann⁽⁴¹⁾ first extensively studied it with a single crystal precession camera method of X-ray diffraction, but their analysis appears not to be fully quantitative, because neither the influences of other variants of the ζ'_2 martensite were eliminated, nor the R-factor as to the atomic parameters estimated by density method was described. A re-examination on the crystal structure by the present authors⁽⁴²⁾ was also qualitative, because it was based on electron diffraction. Ohba *et al.* succeeded in making a single variant of the ζ'_2 martensite by stress inducement in a Au–49.5 at.%Cd alloy single crystal specimen, carefully preventing twinning which was easily introduced into the martensite. Crystal structure of the martensite was examined by means of a single crystal four-circle X-ray diffraction method. As a result, it turned out that the crystal structure was trigonal with $a=0.8095$ and $c=0.57950$ nm, and the space group was $P3$, contrary to the previous result, i.e., $P31m$ ⁽⁴¹⁾. It is interesting to note that the ζ'_2 martensite does not possess center of symmetry. The positions of 18 atoms contained in the unit cell are shown in Table 2, and the crystal structure is schematically shown in Fig. 3. The refinement of the atomic parameters was made up to 7.8% in the R-factor (4.1% in the weighted R-factor), and hence the crystal structure is conceivable to be an ultimate one. According to Ohba *et al.*⁽³⁸⁾, the characteristics of the atomic shuffles, which are largely different from those derived by Vatanayon and Hehemann⁽⁴¹⁾, can be reproduced by the combination of three atomic displacement waves corresponding to $\{110\}\langle 1\bar{1}0 \rangle$ type transverse acoustic waves in the B2 parent phase. The assumption of this type of lattice displacement waves appears reasonable because thermal diffuse scattering of X-rays corresponding to them has been in fact observed in the B2 parent phase⁽⁴³⁾.

As pointed out previously⁽⁴¹⁾, diffraction patterns from

Table 2 Atomic parameters for the ζ'_2 martensite in a Au–Cd alloy identified by Ohba *et al.*⁽³⁸⁾

Site	x	y	z
Au(1a)	0,	0,	0
Au(1b)	1/3,	2/3,	0.151(2)
Au(1c)	2/3,	1/3,	0.000(1)
Au(3d)	0.3333(9),	−0.0192(8),	0.416(1)
Au(3d)	0.6921(7),	0.0253(7),	0.708(2)
Cd(1a)	0,	0,	0.507(3)
Cd(1b)	1/3,	2/3,	0.650(4)
Cd(1c)	2/3,	1/3,	0.506(3)
Cd(3d)	0.335(2),	−0.022(2),	0.913(3)
Cd(3d)	0.680(1),	0.014(1),	0.211(3)

Fig. 3 Crystal structure of the ζ'_2 martensite in a Au–Cd alloy, identified by Ohba *et al.*⁽³⁸⁾

the ζ'_2 martensite are at a glance similar to those from the R phase in Ti–Ni alloys described above, as far as the positions of reflections in reciprocal lattice are concerned. But, whether or not the crystal structures of these two martensites are in fact identical to each other remains unclear, and thus has to be closely investigated. On the other hand, one will see that the crystal structure of the ζ'_2 martensite is entirely different from the γ'_2 one representative of a Au–47.5 at.%Cd alloy, as will be described later. This seems to be rather strange, considering the slight difference in composition between the two alloys. Such a strong composition dependence of crystal structure of martensite in the β phase Au–Cd alloy would also be necessary to be examined from a microscopic point of view.

(2) 2H type martensites in Cu-Al-Ni and Au-Cd alloys

It is now generally accepted that the thermally induced γ'_1 martensite in β phase Cu-Al-Ni alloys possesses a 2H type long period stacking order structure. But, strictly speaking, there were still some uncertainties in the crystal structure with respect to the space group, atom positions and site occupancies of the excess Al and Ni atoms. The latter two points appear in particular to be crucial problems in connection with the rubber-like behavior (or twinning pseudoelasticity), which was found in the Cu-Al-Ni alloys aged in the martensitic state⁽⁴⁴⁾. In order to make these points clear, Ye *et al.*⁽⁴⁵⁾ carried out a thorough crystal structure analysis on the γ'_1 martensite using conventional X-rays and synchrotron radiations. They made a single variant crystal of the γ'_1 martensite by stress induction in a Cu-27.14Al-3.64Ni (at.%) alloy crystal. Precession photographs from the single crystal of the martensite revealed the space group to be $Pnmm$, which was in agreement with that reported by Kurdjumov *et al.*⁽⁴⁶⁾ The lattice parameters of the orthorhombic lattice were determined by a four-circle X-ray diffractometer to be $a=0.43896$, $b=0.53424$ and $c=0.42244$ nm. The atomic parameters as to 8 atoms involved in the unit cell were analyzed by the least-squares fitting under the following assumption: In the basal plane as shown in Fig. 4, Al atoms fully occupy site I and the extra ones do site II; Ni

atoms occupy site III; Cu atoms occupy the rest of sites II and III. The atomic parameters determined are shown in Table 3, for which the R-factor of 6.4% (5.9% in the weighted R-factor) was obtained. The arrows in Fig. 4 indicate exaggeratedly the shifts of atoms from the ideal 2H positions. Next, the site occupancies of the Ni and Al atoms, which are off-stoichiometric from Cu_3Al , were examined from intensity data collected with various synchrotron radiations near K-absorption edges of Cu and Ni atoms. As a result, it was concluded that the distribution assumed as above is the most reliable one.

The single crystal four-circle X-ray diffraction method was also applied by Ye⁽⁴⁷⁾ to the aging problem in the Cu-Al-Ni martensitic alloys. Crystal structure of the γ'_1 martensite was closely examined before and after aging for seven months. Unexpectedly, however, no indication for reordering was found, nor for atomic shift after aging. It is then interesting to examine whether or not this is true in another alloy systems, such as Au-Cd⁽⁴⁸⁾, Cu-Au-Zn⁽⁴⁹⁾ and Cu-Zn-Al⁽⁵⁰⁾, where the rubber-like behavior was also found to occur upon martensite aging. Some significant structural changes were in fact found in the latter two alloys, as will be described later.

The γ'_2 martensite in Au-Cd alloys is widely known as the one which the phenomenological crystallographic theory of the martensitic transformations is successfully applied to⁽⁵¹⁾, and which is first found to be closely related with the rubber-like behavior due to a reversible twin boundary movement after the stabilization upon aging⁽⁵²⁾. However, the atomic parameters in the orthorhombic unit cell of the γ'_2 martensite had not been fully quantitative, because the intensity data of reflections had been acquired so far through powder X-ray or electron diffraction. Ohba *et al.*⁽⁵³⁾ thus made a close examination on the crystal structure of the γ'_2 martensite by a single crystal X-ray diffraction method, obtaining a single-crystalline γ'_2 martensite well stabilized under stress. The atomic parameters were finally refined up to 4.8% in the R-factor (5.1% in the weighted R-factor). Ohba *et al.*⁽⁵⁴⁾ also examined critically whether or not the crystal structure of the γ'_2 martensite changes upon aging as so far suggested by several workers⁽⁵⁵⁾. Unexpectedly, however, neither the peak position nor the integrated intensity was found to change during aging and after the movement of twin boundaries in the aged state. Precise crystal structure of the γ'_2 martensite had been in particular of great interest in connection with the occurrence of the rubber-like behavior after aging, because it appeared to

Fig. 4 Crystal structure of the γ'_1 martensite in a Cu-Al-Ni alloy identified by Ye *et al.*⁽⁴⁵⁾, viewed from the [001] direction. The dotted circle represents the Al atom in the second layer. The arrows indicate the relative atom displacements to the Al atoms in the first layer from the ideal 2H position.

Table 3 Atomic parameters for the γ'_1 martensite in a Cu-Al-Ni alloy identified by Ye *et al.*⁽⁴⁵⁾

Al	$0, \frac{1}{3} + 0.0327,$	$0, \frac{1}{2},$	$0, \frac{1}{2}$
Cu1	$0.0003(3),$	$\frac{1}{2},$	0
Cu2	$\frac{1}{3} + 0.0323(7),$	$0,$	$\frac{1}{2}$
	$\frac{1}{2} + 0.0017(4),$	$\frac{1}{4} + 0.00056(8),$	0
	$\frac{1}{2} + 0.0017(4),$	$\frac{3}{4} - 0.00056(8),$	0
	$\frac{5}{6} + 0.0309(6),$	$\frac{1}{4} - 0.00056(8),$	$\frac{1}{2}$
	$\frac{5}{6} + 0.0309(6),$	$\frac{3}{4} + 0.00056(8),$	$\frac{1}{2}$

be caused by some crystal structural change of martensite. The result obtained by Ohba *et al.*⁽⁵⁴⁾ implies that the crystal structural change upon aging, if any, is extremely delicate, being related to some rearrangement of vacancies. Other experimental methods sensitive to local arrangements of atoms would be necessary to be utilized, such as EXAFS and NMR, for this alloy system.

(3) 18R type martensites in Cu–Au–Zn and Cu–Zn–Al alloys

Crystal structure of the martensite in Cu–Au–Zn shape memory alloys near the stoichiometric composition CuAuZn_2 had been examined by several workers^{(56)–(58)} by means of powder X-ray and electron diffraction. It is now generally accepted that the martensite possesses a long period stacking order structure of the M18R type. However, the atomic configuration in the basal plane had been controversial with respect to the site occupancies of Cu and Zn atoms. The present authors thus investigated it by means of electron channeling enhanced microanalysis⁽⁵⁹⁾. This technique, called ALCHEMI (Atom Location by CHanneling Enhanced Microanalysis) recently developed by Spence and Taftø⁽⁶⁰⁾, is useful for distinguishing the sites occupied by Cu and Zn atoms in the basal plane, which is in general difficult through conventional X-ray and electron diffraction because of the similar atomic scattering factors of these atoms for X-rays and electrons. However, since the site occupancies of all the constituent atoms cannot be uniquely determined by ALCHEMI alone, powder X-ray diffraction was complementarily carried out for this purpose. ALCHEMI was performed on a Cu–26Au–45Zn (at.%) martensitic alloy well-stabilized at room temperature under planar channeling conditions for the (020) plane of the M18R martensite, using an analytical electron microscope, equipped with a field emission type electron gun, operated at 100 kV. Three kinds of atomic sites, I, II and III, were defined in the basal plane, as shown in Fig. 5 for convenience in a quantitative analysis of ALCHEMI. As a result, it turned out that the atomic configuration in the basal plane of the well-stabilized

martensite is consistent with that directly derived from the L2_1 parent phase proposed by Duggin and Rachinger⁽⁵⁶⁾, as shown in Fig. 5(a), as far as the result of ALCHEMI is concerned.

The distribution of Cu and Au atoms into sites I and III became possible to be determined easily by conventional powder X-ray diffraction on the basis of the knowledge obtained from ALCHEMI. In fact, intensity measurements by powder X-ray diffraction revealed that the degree of order for ordering between the mixture of Cu and Au atoms at sites I and III and Zn atoms at site II is almost unity, but that for ordering between Au atoms at site I and Cu atoms at site III is roughly 0.8, as schematically shown in Fig. 5(b). The former ordering corresponds to the nearest neighbor (nn) ordering and the latter to the next nearest neighbor (nnn) one in the L2_1 parent lattice. It was verified that both the nn and nnn orders in the L2_1 parent phase are perfect even when rapidly quenched, as will be described later. The perfect order in the parent phase should be inherited in the martensite because of the diffusionless nature of the martensitic transformation. The observed disordering in the martensite was thus considered to have occurred during aging in the martensitic state. It was then concluded that the origin of the stabilization of martensite, i.e., rises of the reverse transformation temperature is nothing but this type of disordering upon martensite aging. The origin of the rubber-like behavior in this alloy was speculated on the basis of this fact⁽⁵⁹⁾.

The interchange between nearest neighbor atoms was previously suggested by Abu Arab and Ahlers⁽⁶¹⁾ to be responsible for the stabilization of the M18R martensite in Cu–Zn–Al alloys. According to them, Cu and Zn atoms at sites II and III, respectively, in the present notation interchange during martensite aging, resulting in a decrease in long range order. But no evidence was provided by them from the crystallographic point of view. Very recently the interchange between Cu and Zn atoms in the Cu–Zn–Al alloy was directly verified by Nakata *et al.*⁽⁶²⁾ by means of ALCHEMI. They examined the atomic distribution in the M18R martensite of a Cu–11.2Zn–17.1Al (at.%) alloy step-quenched (once quenched into oil bath at 423 K after betatization, kept for 2 min and then quenched into iced water) as a function of aging time up to 56 d at 373 K below its A_s temperature (383 K). With this prolonged aging the martensite was well stabilized. As a result, it turned out that the fraction of Zn atoms occupying the atomic planes consisting of the sites I and III changed from 0.8 to 0.6–0.7 with increasing aging time. On the other hand, the martensite formed upon direct quenching into iced water, which did not transform back into the parent phase by 473 K, exhibited the fraction of about 0.6. The difference in the fraction, k , experimentally determined was slight, but it certainly exceeded the error involved. Accordingly it was concluded that the stabilization of martensite is due to the disordering between Cu and Zn atoms at sites II and III, respectively, as suggested by Abu Arab and Ahlers⁽⁶¹⁾.

The ALCHEMI method has thus turned out to be

Fig. 5 Atomic configurations in the basal plane of the M18R Cu–Au–Zn martensite unaged, (a) and well stabilized, (b), which were identified by the present authors⁽⁵⁹⁾.

useful in the structural analysis especially for the alloy systems consisting of atoms with similar atomic scattering factors like Cu and Zn. When one makes such a structural analysis by means of X-ray diffraction, characteristic X-rays with suitable wave lengths have to be selected so that the anomalous dispersion effects in atomic scattering factors can be utilized, as in fact Ye *et al.*⁽⁴⁵⁾ did for a Cu–Al–Ni alloy. However, in general it is not easy to obtain X-rays relevant to this aim with a sufficiently high intensity. Ye *et al.* thus utilized the synchrotron orbital radiations with extremely high intensities. Taking into account of this situation, the ALCHEMI method is simple and can easily be carried out through analytical electron microscope. Moreover the results are sufficiently reliable as far as ALCHEMI is performed carefully, taking several factors into account⁽⁶³⁾. Another example of the structural analyses by ALCHEMI will be shown later. It is interesting to compare the results obtained by the simple ALCHEMI with those by straightforward diffraction methods.

(4) 7R type martensite in β phase Ni–Al alloys

It is now established that the β phase Ni–Al Alloys with 62 ~ 64 at.%Ni undergo the B2 to L1₀ martensitic transformation in a temperature range between around 77 K and ambient temperature. However, another martensite with a seven-layer structure was found by Enami *et al.*⁽⁶⁴⁾ slightly above M_s temperature. It is interesting to note that according to a neutron scattering experiment by Shapiro *et al.*⁽⁶⁵⁾, the phonon dispersion curve of the $\langle \zeta \zeta 0 \rangle$ transverse acoustic branch (displacements along $\langle 110 \rangle$) for an alloy with 62.5 at.%Ni shows a marked but incomplete softening at around $\zeta = 1/6$ as temperature falls down to its M_s temperature about 80 K. Martynov *et al.*⁽⁶⁶⁾ examined in more detail crystal structure of the martensite stress-induced as well as thermally formed by single crystal X-ray oscillation photograph method. As a result, they found that the crystal structure was a 7R(52) type long period stacking order structure, and that it was monoclinic because of a relative shift from an ideal position ($\pm a/3$) of the adjacent basal planes due to the atomic order⁽⁶⁷⁾. Lattice parameters of the 7R martensite were determined to be $a = 0.418$, $b = 0.271$, $c = 1.448$ nm and $\beta = 94.3^\circ$, and the relative shift between the adjacent basal planes to be $19a/42$ or $-16a/42$ in the monoclinic coordinate system. They also found that the martensite was transformed into the L1₀ type one by stressing under an appropriate condition.

Recently Noda *et al.*⁽⁶⁸⁾ made a re-examination of the crystal structure of the 7R martensite by means of single crystal neutron diffraction, and found that the superlattice reflections characteristic of the 7R martensite exhibit the following anomalies: The position was almost, but not exactly, at $n/7$ of the distance between the origin and the reflections from $\{110\}$ planes of the B2 parent phase; the peak shape was broadened along the c^* direction; some peaks had a shoulder peak or even split into double peaks. When the shifts and broadening were ignored, the

approximate lattice parameters of the 7R martensite were almost identical to those by Martynov *et al.*⁽⁶⁶⁾. Assuming the basal plane to be rigid and the space group to be $P2/m$, the three independent positional parameters involved in the ABACBACA sequence were refined by the least-squares fitting up to 14.1% of the R-factor, the values of them being listed in Table 4, while the R-factor for the positional parameters by Martynov *et al.*⁽⁶⁶⁾ was 20.5%.

Noda *et al.*⁽⁶⁸⁾ ascribed the observed anomalies in the superlattice reflections to the coexistence of two monoclinic lattices with different monoclinic angles, $\beta^{(1)} = 94.37^\circ$ and $\beta^{(2)} = 93.82^\circ$, i.e., a two-monoclinic-mixed state. According to Yamada *et al.*⁽⁶⁹⁾, this state corresponds to the crest-riding-periodon (CRP) phase recently proposed by Barsch and Krumhansl⁽⁷⁰⁾. The CRP is defined as a metastable phase in the phenomenological Ginzburg-Landau type free-energy functional, where the order parameter spatially oscillates between two different values. According to Yamada *et al.*⁽⁶⁹⁾, the observed mixed state was consistent with the predicted CRP phase, where two differently strained lattices with different internal displacement parameters coherently coexist. In fact, the observed features of the shift and broadening were fairly well reproduced by the two-monoclinic-mixed state model. Their explanation seems thus to be attractive, but a transmission electron microscopy (TEM)⁽⁶⁴⁾ of the 7R martensite clearly showed the existence of a high density of random stacking faults on the basal plane, as in other martensites with long period stacking order structures, and thus the shift and broadening of reflections might be simply brought about by the random stacking faults. From an experimental point of view, it seems that a high resolution X-ray diffraction experiment is necessary to be made using a much smaller single-crystalline 7R martensite than that used for the neutron diffraction study.

Very recently Khachaturyan *et al.*⁽⁷¹⁾ interpreted the appearance of the 7R martensite in terms of the adaptive martensite. According to them the 7R martensite, which is an intermediate phase in the course of the B2 to L1₀ martensitic transformation, is a twinned martensite consisting of two variants of the L1₀ martensite twin-related on its $\{111\}$ plane⁽⁷²⁾ in a microscopic scale, the micro-twinned martensite being called the adaptive martensite. If so, however, the adaptive martensite is merely a faulted tetragonal one and cannot be a phase in the thermodynamical sense. It is well established⁽⁷³⁾⁽⁷⁴⁾ that the Cu–Al–Ni martensites with 2H, 18R₁, 18R₂ and 6R type

Table 4 Stacking positions of basal planes along the x direction in the ABACBACA sequence of the 7R martensite determined by Noda *et al.*⁽⁶⁸⁾

0th	0	0
1st	x_1	0.4656(3)
2nd	x_2	0.0731(6)
3rd	x_3	0.6921(1)
4th	$1 - x_3$	0.3078(9)
5th	$1 - x_2$	0.9268(4)
6th	$1 - x_1$	0.5343(7)

long period stacking order structures possess their own definite stress-temperature regions where they are thermodynamically stable. Although the phase diagram in stress-temperature coordinate has not been established yet for the Ni–Al alloy system, a similar phase diagram to that in the Cu–Al–Ni alloy system may hold in the former alloy system. In other words, there may be a possibility that the 7R martensite is also a definite phase like in the Cu–Al–Ni alloy. Since the formation of the adaptive martensite does not generate a volume-dependent elastic energy, the difficulty of the nucleation of martensite may be overcome with the adaptive martensite, but it appears that their idea is basically inadequate in the above sense.

3. Fe-based alloys

(1) Two-tetragonal-mixed state in Fe–Pd alloys

In Fe–Pd alloys around 30 at.%Pd three kinds of martensites have so far been well-known to exist, depending on composition, i.e., bcc in the compositions less than about 27.5 at.%Pd, bct between about 27.5 and 30.5 at.%Pd and fct between 30.5 and 32.0 at.%Pd⁽⁷⁵⁾. Among them only the fct martensite is thermoelastic⁽⁷⁶⁾⁽⁷⁷⁾, and prior to the formation some anomalous phenomena such as tweed contrast and diffuse streaks in transmission electron microscopy and so on are reported to take place well above M_s temperature^{(78)–(80)}. The tweed contrast is believed to be due to the formation of small platelike fct nuclei in the parent phase⁽⁷⁸⁾. Recently Seto *et al.*⁽⁸¹⁾ closely examined crystal structure of the parent phase in the very vicinity of the fcc to fct transformation temperature by means of precise X-ray diffraction as well as neutron diffraction. As a result, they found that an intermediate phase exists in a very narrow temperature range of only about 8 K above the fcc to fct transformation temperature 265 K for an Fe–30.1 at.%Pd alloy single crystal, and that it consists of two kinds of tetragonal lattices with different tetragonality: Lattice parameters of the two lattices were $a_1=0.3795$, $c_1=0.3648$ nm ($c_1/a_1=0.961$) and $a_2=0.3766$, $c_2=0.3737$ nm ($c_2/a_2=0.992$) at 267.5 K. Figure 6 shows a temperature dependence of the lattice parameters calculated from the observed peak positions around the 600 reflection of the parent phase. It seems rather strange in Fig. 6 that the lattice parameter, c_1 , is missing. This was explained to be due to an experimental condition that the incident beam divergence was set very small in the high resolution spectrometer and so the irradiated area did not include areas giving rise to the corresponding reflection. Since such an intermediate phase was also observed by neutron diffraction, they considered it to exist throughout the whole crystal volume.

According to Seto *et al.*⁽⁸¹⁾ the observed mixed state of two tetragonal lattices is not a simple incoherent mixture of the two different phases, but a coherent coexistence of them, and the appearance of the two-tetragonal-mixed phase is understandable in terms of the CPR phase as for the 7R martensite in Ni–Al alloys. By the way, Sugiyama *et al.*⁽⁷⁵⁾ observed a strong temperature dependence of the tweed contrast in TEM image and a remarkable enhance-

Fig. 6 Temperature dependence of the lattice constants of the parent, the two-tetragonal-mixed phase and the fct martensite in an Fe–Pd alloy observed by Seto *et al.*⁽⁸¹⁾ T_1 (273 K) and T_2 (265 K) stand for the temperatures where the new intermediate phase and the fct martensite appear, respectively.

ment near M_s temperature of the fcc to fct transformation on cooling. According to them, the tweed contrast is due to the formation of the variant mosaic structure, which consists of small platelets of the fct nuclei: four fct variants whose c axes are nearly parallel to one of the three cubic axes of the parent lattice are formed so as for the elastic energy in the parent lattice to be minimized. Fujita⁽⁸²⁾ showed that the mixed state of the fct nuclei and the fcc parent phase reduces the total free energy of the system by the amount of entropy of mixing, and that the transition from fcc to fct exhibits a second order-like nature as a consequence. The appearance of the two-tetragonal-mixed phase is abrupt, but that of the variant mosaic structure seems continuous. It is thus not clear whether the two states are identical to each other or not.

Khachatryan *et al.*⁽⁷¹⁾ applied their adaptive martensite model also to the intermediate phase in the Fe–Pd alloys. They calculated the lattice parameters of the pseudo-orthorhombic adaptive martensite, a_{ad} , b_{ad} , c_{ad} , in the temperature range between T_1 and T_2 in Fig. 6 from those of the parent and the “normal” fct martensite. Since a_1 , a_2 and c_2 in Fig. 6 were reproduced by the calculated a_{ad} , b_{ad} and c_{ad} , respectively, they regarded the intermediate phase as the adaptive martensite. As described above, however, the intermediate phase is a two-tetragonal-mixed state according to the precise diffraction experiment by Seto *et al.*, not such a pseudo-orthorhombic single phase as predicted from the adaptive martensite model. The experimental facts should be taken into account seriously in the theoretical consideration.

(2) Thermoelastic Fe–Pt tetragonal martensite

Crystal structure of the non-thermoelastic martensite in a partially ordered Fe₃Pt alloy had been identified by the present authors⁽⁸³⁾ to be a specific ordered structure expected from the Bain distortion of the $L1_2$ type austenite lattice by means of electron diffraction: The unit cell is quadruple to the fundamental bcc one. However, the

present authors found anomalous extra reflections from the thermoelastic martensite in a well-ordered Fe-24 at.%Pt alloy in the low temperature electron diffraction, which could not be explained at all by the above ordered structure⁽⁸⁴⁾. The extra reflections appeared systematically at reciprocal lattice points hkl , where $h+k$ and l were simultaneously half integers when referred to the fundamental bct lattice, and they were much weaker than the superlattice ones. The appearance and disappearance of the extra reflections were completely reversible in the subzero temperature range, and no violation of atomic order was found in the L_{12} parent phase after the reverse transformation. Electron diffraction patterns showed the weighted reciprocal lattice to belong to the Laue group $4/mmm$. Then, assuming the space group $\bar{I}4m2$, a structural model with a unit cell twice as large as that of the ordered structure in the direction of the c axis was tentatively proposed, as shown in Fig. 7. To be noted here is that Fe atoms are shuffled in a complicated manner. The complicated atomic shuffles would not be unexpected, because the parent lattice is not primitive and hence all the final atomic positions cannot be defined by the Bain distortion alone. The origin of the complicated shuffles of Fe atoms is not understood from the crystallographic point of view, and then it may be due to some magnetic origin. Two atomic parameters, x and z , to be determined in this structural model should be different from $1/4$ and 0 , respectively, because if not, the crystal structure becomes identical to the former one. Then, assuming some proper values for x and z , the intensity distribution in reciprocal lattice was calculated. As a result, it turned out that the structural model reproduced well the observed intensity distribution qualitatively. For the quantitative analysis, a single crystal X-ray diffraction method will be necessary to be made.

(3) Unusual structure of γ -Fe precipitate in Cu matrix

The γ phase of pure Fe is stable only at high temperatures between 1185 and 1667 K under normal pressure, but it can be retained even at room temperature in Fe precipitates formed in supersaturated Cu-Fe alloys by appropriate heat treatments⁽⁸⁵⁾. It is well-known that the γ -Fe precipitates undergo the fcc to bcc martensitic transformation when plastically deformed⁽⁸⁶⁾, extracted from the Cu matrix⁽⁸⁷⁾ or in thin foil specimens⁽⁸⁸⁾. Recently, however, another structural phase transformation, i.e., a cubic to tetragonal one, was found to take place in the γ -Fe precipitates when subzero cooled. Tsunoda and Kunitomi⁽⁸⁹⁾⁽⁹⁰⁾ studied the phase transformation extensively by single crystal X-ray and neutron diffraction at low temperatures. They prepared a Cu-2.8 at.%Fe alloy single crystal and aged it at a temperature between 923 and 1073 K for various periods after the solution-treatment at 1272 K for 5 h followed by water quenching. The particle size of the γ -Fe precipitates was 50~60 nm in diameter for a representative case where the alloy was aged at 923 K for 90 h. The tetragonal lattice was formed below 70 K with 0.17% contraction along one of the

Fig. 7 Tentative model for crystal structure of the thermoelastic martensite in an ordered Fe-Pt alloy by the present authors⁽⁸⁴⁾. Small letters are the Wyckoff notation for the atom positions in the space group $\bar{I}4m2$.

cubic axes and 0.19% expansions along two directions in the plane perpendicular to it "on average". They found the existence of a temperature region where the two phases of cubic and tetragonal lattices coexisted, and of a thermal hysteresis of about 7 K between the forward and the reverse transformations upon cooling and heating, respectively. Consequently this phase transformation could be martensitic in nature. Another striking phenomenon was that satellite reflections appeared simultaneously along the $\langle 110 \rangle$ and $\langle \bar{1}\bar{1}0 \rangle$ directions perpendicular to the unique $\langle 001 \rangle$ axis accompanying the lattice change. The appearance of the satellites was consistent with the occurrence of a lattice modulation with the $\{110\}\langle 1\bar{1}0 \rangle$ type lattice displacement waves in the tetragonal lattice. The wave length, λ , of the lattice modulation was determined from the satellite position to be 11.24 nm, and the displacement amplitude, Δ , which depended on temperature, to be 0.0047 nm from their intensities at 10 K. It is interesting to note that the displacement amplitude, about 1.3% of the a axis, is much larger than the contraction along the c axis upon the transformation, as seen from Table 5, where all the crystallographic parameters obtained are summarized. Because of this, the resulting local lattice structure, as

Table 5 Lattice constants of the tetragonal structure of the γ -Fe precipitate with a lattice modulation in Cu matrix determined by Tsunoda and Kunitomi⁽⁸⁹⁾.

a_0 (68 K)	=0.3557 nm
a (10 K)	=0.3584 nm
$a^+ = a_{\max}$	=0.3631 nm
$a^- = a_{\min}$	=0.3537 nm
c (10 K)	=0.3571 nm
c/a (10 K)	=0.9964
a^-/a^+ (10 K)	=0.9741

a_{Cu} = 0.3603 nm at 10 K is used as a reference.

shown in Fig. 8, is approximately orthorhombic at the node of the periodic lattice wave and tetragonal at the antinode. It was found that there exists a critical size for the γ -Fe particles to undergo such a phase transformation as above: The critical value was estimated to be roughly 15 nm, and the particles smaller than it did not undergo the transformation. Tsunoda *et al.*⁽⁹¹⁾ observed magnetic satellite reflections of γ -Fe precipitates in neutron diffraction, corresponding to such a lattice modulation. It was thus concluded that the structural phase transformation accompanying the lattice modulation is not limited to the specimen surface, but is one as a bulk property.

The origin of the cubic to tetragonal transformation seems to lie in the antiferromagnetic transition in the γ -Fe precipitates, because according to Tsunoda *et al.*⁽⁹⁰⁾, the Néel temperature coincides with M_s temperature. But, the situation appears not to be so simple, because the γ -Fe precipitates about 15 nm in size did undergo the antiferromagnetic ordering at about 50 K, but they did not the structural phase transformation. On the other hand, the origin of the lattice modulation in the γ -Fe precipitates was ascribed to the formation of a twin boundary associated with the martensitic transformation, the twin boundary being formed by the lattice deformation wave without the interface dislocations. This type of twin boundary was recently proposed by Barsch and Krumhansl⁽⁹²⁾ theoretically. It is to be noted, however, that the lattice modulation proposed by Barsch and Krumhansl takes place so that the c axes of two variants of the tetragonal martensite make approximately a right

Fig. 8 Schematic illustration of the low-temperature lattice structure of a γ -Fe precipitate in Cu matrix, identified by Tsunoda and Kunitomi⁽⁸⁹⁾, viewed from the [001] direction.

angle to each other, lying in a plane perpendicular to the twinning plane. In the γ -Fe precipitates only one of three variants was associated with the lattice modulation. Hence it appears that the lattice modulation has nothing to do with the minimization of strain energy associated with the Bain strain, although the lattice modulation itself with a displacement amplitude much larger than the tetragonal distortion occurs so as for the strain energy to be minimized. Thus, the origins of the unusual structural phase transformation and the lattice modulation remain unsolved yet.

It was recently reported⁽⁹³⁾ that the γ phase of Fe-Ni alloys which normally undergo the fcc to bcc martensitic transformation above room temperature in bulk state can be retained in ultrafine unconstrained particles (20–200 nm in diameter) even at 77 K. Whether or not such a fine unconstrained γ particle also undergoes the unusual phase transformation as found in the γ -Fe precipitates at lower temperature may be crucial for understanding the origin of the latter.

III. Refined Crystal Structures of Parent Phases

1. $D0_3$ type parent phase in Cu-Al-Ni alloys

Crystal structure of the γ'_1 martensite of the β phase Cu-Al-Ni alloys described in the section II-(2) suggests that the excess Al and Ni atoms in the parent lattice with the $D0_3$ type as shown in Fig. 9 occupy the Cu(2) site and the Cu(1) site, respectively[†]. However, according to Nakamura *et al.*⁽⁹⁴⁾ and Kajitani *et al.*⁽⁹⁵⁾, excess Ni and Al atoms occupy both the Cu(1) and Cu(2) sites, and are rearranged into the Cu(2) site upon aging. The latter rearrangement of atoms is nothing but ordering from $D0_3$ to $L2_1$, to which Nakamura *et al.* ascribed a rise of M_s during aging. Which of the Cu(1) and Cu(2) sites is

Fig. 9 Atom configuration in the unit cell of the $D0_3$ type Cu_3Al crystal.

[†] Note that the Cu(1) and Cu(2) sites defined in Fig. 9 correspond to those in the γ'_1 martensite, which are in inverse relation with those defined in Fig. 4.

preferentially occupied by the Ni atoms could be examined by X-ray diffraction method utilizing the anomalous dispersion effects or neutron diffraction method. Nakata *et al.*⁽⁹⁶⁾, however, simply adopted the ALCHEMI method to this problem, and showed that it is effective for such an examination, as described below.

A Cu-28.6Al-3.7Ni (at.%) alloy single crystal was made, and disk-shaped specimens whose surface plane were nearly parallel to a $\langle 100 \rangle$ direction were subjected to the following three kinds of heat-treatments after betatization: (a) quenching into a 10% NaOH solution at 263 K, (b) quenching into hot water at 363 K, and (c) aging at 523 K for 1h after the heat-treatment (b). ALCHEMI was carried out on these specimens under planar channeling conditions for a $\{200\}$ plane of the parent lattice. The fraction of Ni atoms occupying the Cu(2) site, k , was measured for the three kinds of specimens, and are shown in Table 6. Since the obtained values of k were substantially zero for the three kinds of specimens, it was concluded that almost all of the Ni atoms occupy the Cu(1) site regardless of the heat-treatments. The preferential occupancy of the Ni atoms at the Cu(1) site is consistent with the crystal structure of the γ' martensite proposed by Otsuka *et al.*⁽⁹⁷⁾ and Ye *et al.*⁽⁴⁵⁾ as described in the section II-(2). It is interesting to note that there is no difference in the fraction k among the specimens (a), (b) and (c), although their M_s temperatures were largely different from each another (158, 185 and 259 K, respectively). It is also to be noted that the Cu(1) and Cu(2) sites are proved not to be crystallographically equivalent with respect to the occupancy by Ni atoms. In this sense, strictly speaking, the parent lattice is not of the $D0_3$ type as frequently designated so far, but of the $L2_1$ type. The result thus indicates that the increase in M_s is not due to the ordering from $D0_3$ to $L2_1$ as suggested by Nakamura *et al.*⁽⁹⁴⁾, but possibly to the further progress in nnn ordering between the Al site and the Cu(2) site in the $L2_1$ parent lattice. The consistency as to the site occupancy between the results obtained by Nakata *et al.* and others demonstrates that ALCHEMI is a simple, but an effective technique for crystal structural analysis to which conventional X-ray and electron diffraction is difficult to be applied.

ALCHEMI was also applied successfully to the determination of site occupancies of Cu and Zn atoms in the $L2_1$ type parent lattice of a Cu-21Au-45Zn (at.%) shape memory alloy by the present authors⁽⁹⁸⁾. As described in the section II-(2), the problem remaining unsolved in this alloy system had been the site occupancies of Cu and Zn atoms in the M18R martensite and thus in the $L2_1$ type parent lattice as well. Our ALCHEMI experiment show-

ed that Zn atoms are located at the body-center sites, while Cu atoms were at the corner sites, referring to the fundamental bcc lattice. This structure was in agreement with the $L2_1$ type one proposed by Duggin and Rachinger⁽⁵⁶⁾. On the basis of this result obtained by ALCHEMI, a further structural analysis was performed through powder X-ray diffraction, and it was shown that not only the nn ordering but also the nnn ordering is completed in the present alloy even when rapidly quenched after betatization. This result was in contrast with that for a Cu-Al-Ni alloy rapidly quenched where the nnn ordering was incomplete while the nn ordering was completed⁽⁹⁹⁾. The remarkable increase in M_s of the Cu-Al-Ni alloys slowly quenched and subsequently aged was thus attributed to the increase in the degree of nnn ordering. The complete $L2_1$ ordering in the Cu-Au-Zn alloy was consistent with the fact that M_s temperature was hardly changed by the quenching rate and subsequent aging. It was thus proved from the precise structural analyses that the change in transformation temperature, which is one of aging effects in the Cu-based shape memory alloys, can be understood in terms of atomic ordering.

2. B2 type parent phase in Ti-Ni-X alloys

It is widely known in Ti-Ni shape memory alloys near equiatomic composition that not only the martensitic transformation temperature but also the crystal structure of martensite is strongly affected by small addition of third elements such as Fe, Cu and so on. These affections would possibly originate from some changes in the electronic state of the alloys caused by addition of the third elements. Since the electronic state of alloys is expected to sensitively depend on the locations of the third elements, it would be necessary to examine which of the Ni and Ti atom sites in the B2 type parent lattice is occupied by the third elements. However, for example, when a third element is added to a Ti-Ni alloy so as to become the composition of $Ti_{50-x}Ni_{50-x}X_x$ or $Ti_{50-x}Ni_{50}X_x$, it is not obvious that the third element occupies the Ni atom site or the Ti one, respectively. It would be possible that a third element which has a strong interaction with Ni atoms occupies the Ti site even in the composition of $Ti_{50}Ni_{50-x}X_x$ and *vice versa*. Thus the site occupancy of the third elements in the Ti-Ni alloys is needed to be experimentally examined. ALCHEMI may be applicable to this kind of problem, and in fact, it was proved by Nakata *et al.*⁽¹⁰⁰⁾⁽¹⁰¹⁾ that the site occupancy of third elements with small additions can be determined by ALCHEMI with a sufficient accuracy, as described below.

Various ternary alloys with compositions of $Ti_{50-x}Ni_{50}X_x$ (alloy A), $Ti_{50-x/2}Ni_{50-x/2}X_x$ (alloy B) and $Ti_{50}Ni_{50-x}X_x$ (alloy C) ($X = \text{Cr, Mn, Fe, Co and Cu}$; $0 < x \leq 3$) were prepared by arc-melting. After homogenization at 1273 K for 24 h, the alloy specimens were quenched into iced water. ALCHEMI was carried out under planar channeling conditions for a $\{100\}$ superlattice plane of the B2 parent lattice. The fraction of a third element occupying the Ni atom site, k , was

Table 6 Fractions of the Ni atoms occupying the Cu(2) site, k , determined through ALCHEMI by Nakata *et al.*⁽⁹⁶⁾ for the three kinds of Cu-Al-Ni alloy specimens differently heat-treated.

Heat treatment	Rapid quenching	Slow quenching	Aging
k	0.11 ± 0.11	0.10 ± 0.08	0.06 ± 0.08

measured for each alloy in a similar way to that described previously. The results are summarized as follows: In the alloy A, Fe and Co atoms occupy preferentially the Ni site in spite of the fact that the alloys are Ni-rich, while Cr atoms occupy both the sites with nearly equal fractions, and Mn and Cu atoms the Ti site. In the alloy B, while Fe and Co atoms are preferentially located at the Ni site, Cr, Mn and Cu atoms are at both the sites with nearly equal fractions. In the alloy C, all the third elements examined occupy the Ni site preferentially. As an example, the values of k obtained for the alloy B are shown in Table 7. It was shown that these features of the site occupancy of the third elements in the B2 lattice can be understood from the thermodynamics based on the Bragg-Williams approximation, taking account of the binding energies between the constituent atoms and the configurational entropy. Since the site occupancy of the third elements in various ternary alloys has been known in this way, how M_s , temperature and also the appearance of the R phase are related to the site occupancy of the third elements should be clarified as the next step.

IV. Closing Remarks

As described above, precise crystal structural analyses have been successfully made recently for several martensites, some of which had remained unsolved for a long time because of their complex structures, and for parent phases as well. We have seen how important to make single crystals of the martensites is, so that single crystal four-circle X-ray diffractometer can be used for the accurate crystal-structural analysis. The accurate temperature control is also very important. It made it possible to find an intermediate phase in Fe-Pd alloys as well as the ghost lattices in Ti-Ni and Au-Cd alloys in a very narrow temperature range of less than 10 K above M_s .

In order to understand the origin and mechanism of the martensitic transformations from a microscopic point of view, the determination of the lattice parameters alone is not enough, but the accurate measurements of all atomic parameters will be necessary, because the microstrain and the electronic state in a unit cell will strongly depend on them. On the other hand, the existence of such an intermediate phase as found in Fe-Pd alloys may serve for understanding the nucleation of martensite. Although useful pieces of knowledge have certainly been accumulated, precise information is still limited. Further progress is hoped in this field of study on the martensitic transformations.

Table 7 Fractions of various third elements occupying the Ni site in the B2 lattice of $Ti_{20-x/2}Ni_{50-x/2}X_x$ alloys determined through ALCHEMI by Nakata *et al.*⁽¹⁰⁰⁾

$Ti_{48.5}Ni_{48.5}X_3$ Alloys	k
Ti-Ni-Co	1.00 ± 0.07
Ti-Ni-Fe	0.89 ± 0.07
Ti-Ni-Mn	0.51 ± 0.07
Ti-Ni-Cr	0.50 ± 0.11
Ti-Ni-Cu	0.52 ± 0.18

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