OVERVIEW

Recent Neutron Scattering Studies on the Premartensitic State of BCC-Based Metals and Alloys

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In the present article, we review the recent neutron scattering studies on the anomalous behaviours found in the premartensitic bcc-based metals and alloys, i.e. alkali metals, group-IV metals, β -phase alloys, Ni-base alloys and others such as T1 and group-III metals. Lattice dynamical anomalies appearing on the $[110]TA_1$ and $[111]LA$ phonon dispersion relations of these materials are discussed from a viewpoint of the martensitic transformation mechanism with referring briefly to theoretical studies. We also consider characteristics of anomalous elastic scatterings associated with the ω phase formation. Concerning these anomalies, we point out the importance of further examinations on the effects of vacancies, anharmonicity and electronic structure.

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I. Introduction

It is now well-defined that the martensitic phase transformation (hereafter abbreviated to MPT) is the first order transformation with diffusion-less or displacive character. Although MPT was first the name to describe a phase transformation occurring in the quenched carbon steels, it is now widely found in many non-ferrous metals and alloys and even in some kinds of compounds, besides ferrous alloys. Among these materials, we will pay our attention in the present overview to several groups that parent phases have the bcc-based structures, i.e. bcc, B2 (CsCl type), $D0_3$ (Fe_3Al type) and $L2_1$ (Heusler type) structures. They are classified into alkali metals, group-IV metals, β -phase alloys based on the noble metals Cu, Ag and Au, Ni-base alloys such as NiTi and NiAl, and others. A common characteristic of these materials is that each martensite has a periodic layer structure: hcp (or 2H), fcc (or 3R) and 9R (or 18R) structures are typical.

Concerning MPT of the bcc-based materials, we need to refer to Zener's prediction⁽¹⁾. He suggested over 40 years ago that the bcc lattice would be destabilized at low temperature because the elastic stiffness constant $C' = (C_{11} - C_{12})/2$ was remarkably small as a result of the ion-exchange interaction. In other words, a large elastic anisotropy defined by $A = C_{44}/C'$ would be responsible for the bcc lattice instability. Such a prediction led many studies to search for low temperature transformation in the alkali metals, and before long Barrett⁽²⁾ found by X-

ray scattering experiments that the Li metal undergoes MPT to the hcp phase when deformed plastically at about 77 K. Later Barrett and Trantz⁽³⁾ proved the bcc to hcp transformation to occur in Li only by cooling to about 70 K. In addition, the X-ray study by Barrett⁽⁴⁾, showed that the bcc Na metal transforms partially to the hcp phase by cooling to 36 K. These results would thus imply that the alkali metals are typical materials undergoing MPT through the Zener mode instability.

The β phase alloys also belong to an appropriate alloy system wearing anomalously high elastic anisotropy. Long ago it has been proved that the anisotropy factor A of the B2 phases of $CuZn$ ⁽⁵⁾⁽⁶⁾ and $AuCd$ ⁽⁷⁾ alloys is very large and increases markedly with decreasing temperature towards each M_s (martensite-start) temperature. This anomaly is due to the cooperative behaviour along the opposite directions each other between the elastic constants C' and C_{44} : temperature coefficient of C' is positive while negative for C_{44} in a wide range of temperature above M_s . Such anomalies have been so far found in many β phase alloys⁽⁸⁾⁻⁽¹⁴⁾.

From the viewpoint of crystal geometry, on the other hand, MPT in the present subject should proceed through the Burgers relation⁽¹⁵⁾ consisting of the (110) $[1\bar{1}0]$ and $(1\bar{1}2)$ $[1\bar{1}\bar{1}]$ shear processes. Since the elastic constant C' is the resistive force to the (110) $[1\bar{1}0]$ shear, the C' softening observed in the parent phase (called usually the β_1 phase) of many β -phase alloys, for example, indicates immediately the lattice instability towards MPT according to the Zener mode. In addition, we found in many β_1 phases a softening of another kind of shear con-

stant to occur⁽¹²⁾⁽¹⁶⁾⁽¹⁷⁾: the constant, named the special mode C_s , corresponds to the $(1\bar{1}2) [1\bar{1}\bar{1}]$ shear. The experimental results obtained so far, however, prove that the softening of both C' and C_s is incomplete and they remain at large values even just above the M_s temperature. The Burgers shears must encounter strong resistance. Therefore we must conclude that the lattice softening mechanism, as found in Nb_3Sn ⁽¹⁸⁾ for example, does not operate in MPT of the β phase alloys. This conclusion is also valid for NiTi ⁽¹⁹⁾⁽²⁰⁾ and NiAl ⁽²¹⁾ alloys. In addition, the Li metal for example behaves as elastically normal material⁽²²⁾⁽²³⁾.

It must be also noticed that Cochran⁽²⁴⁾ proposed “soft mode scheme” nearly 30 years ago as the displacive phase transition mechanism. This concept means that a certain kind of phonon mode tends to zero frequency with approaching the transition temperature. Such an unstable phonon mode is called soft phonon mode. If the soft mode is condensated, the crystal lattice to which the mode belongs becomes unstable and thus results in transformation to the low temperature phase. Since the atomic displacements induced by such a phonon mode in question determine the low temperature structure, the soft mode is just a true precursor of the phase transition. As mentioned above, a typical structure of the martensite found in the bcc-based materials is 2H or 9R (or 18R), and hence the wavelength of the corresponding lattice modulation is 2 or 3 times the $[110]$ repeat distance of the parent lattice. Therefore precursor to be found, if it exists, should appear as phonon energy anomaly in the $[110]\text{TA}_1$ branch at q_0 or $2/3q_0$, where q_0 is defined as the reduced wave vector corresponding to the Brillouin zone boundary. Structural phase transition associated with the soft phonon mode was indeed found, for example, in SrTiO_3 in 1969⁽²⁵⁾.

Phonon dispersion relations of the β_1 -AuCuZn₂ alloy were studied by Mori and others⁽²⁶⁾ by means of neutron inelastic scattering technique. They found that the $[110]\text{TA}_1$ phonon branch[†] is throughout low-lying and accompanied by an anomalous dip near $2/3q_0$. Such a dip, furthermore, was enhanced with decreasing temperature towards M_s . They suggested a possibility that the dip results from the enhanced Kohn anomaly⁽²⁷⁾⁽²⁸⁾. Since the β_1 -AuCuZn₂ alloy transforms to the 18R martensite, it seems natural to attribute the $2/3q_0$ dip to a precursor phenomenon of MPT. However, we are faced with a serious question for the following reasons. First, the phonon energy at the dip never completely falls down to zero even at the M_s temperature. Second, the $2/3q_0$ dip is also found in the $[110]\text{TA}_1$ phonon branch of the β_1 -CuAlNi alloy⁽²⁹⁾: the alloy transforms to the 2H martensite and the wave with q_0 should be responsible for such a lattice modulation. At least, it is evident that the soft phonon mode is not acceptable for the MPT mechanism

in the β phase alloys.

As presented later, recent lattice dynamical studies on the bcc group-IV metals and others have revealed the existence of strongly damped and temperature dependent phonon modes which have been considered to be precursor fluctuation: phenomena are markedly different from those of the alkali metals and the β -phase alloys. Under these circumstances, it is very important to summarize lattice dynamical behaviours revealed by the recent neutron studies on the premartensitic state of many metals and alloys. We must examine whether phonon anomalies, and also associated elastic diffuse scatterings, observed so far in many materials are due to a common origin or not, and especially whether such anomalies are relevant to the mechanism of MPT, because the origin of MPT is not yet proved. In the present overview, we will survey briefly the results obtained by the recent neutron studies on the premartensitic state of the materials mentioned above, and then discuss what is essential phenomenon behind the anomalies.

It must be emphasized here that neutron scattering technique is invaluable probe to study both static and dynamic properties of phase transformations. Regarding neutron scatterings by solids, we can separate pure elastic component from diffuseness due to lattice vibrations of atoms, and hence we can observe precisely static lattice distortion associated with phase transformations like MPT. Inelastic neutron scattering method is the only probe to measure phonon energies over entire Brillouin zone of solids. In addition, the neutron scattering method is also adequate for high or low temperature experiments with furnace or cryostat because of very small absorption of thermal neutrons for solids research. Therefore it is clear that the neutron scattering technique is quite relevant to examine the problem whether MPT is accompanied by static and dynamic precursor phenomena.

II. Alkali Metals

As mentioned above, the X-ray studies⁽²⁾⁻⁽⁴⁾ implied that the alkali metals are typical materials undergoing MPT along the Zener mode instability⁽¹⁾. Furthermore, the alkali metals have commonly very simple electronic structure and exhibit nearly free electron behaviour⁽³⁰⁾. They have nearly spherical Fermi surface which lies well inside the first Brillouin zone. Such situations would give us a considerable motivation to better understand the nature of the Zener mode instability of these metals.

In the following, we summarize briefly the recent neutron scattering experiments on the alkali metals in connection with the lattice instability and MPT. The neutron studies of precursor effect above M_s , however, revealed no or only a weak softening of the particular phonon branch closely related to MPT. In Li and Na, phonon energies of small wave vectors of the $[110]\text{TA}_1$ phonon branch become even larger when cooled toward M_s . This means the relevant elastic shear constant C' becomes harder. No elastic precursor or charge-density-

[†] We adopt the notation $[110]\text{TA}_1$ in order to represent the transverse acoustic branch with the wave and polarization vectors parallel to the $[110]$ and $[1\bar{1}0]$ directions, respectively, although some literatures have used $[110]\text{TA}_2$ instead of $[110]\text{TA}_1$.

wave (CDW) satellite reflection has been found in Na and K. Although Li shows strong satellite reflections above M_s , they are due to coexistence of the low temperature phase. Theoretical studies associated with MPT of the alkali metals will be also briefly given in this section.

1. Li metal

Based on the X-ray study, Barrett⁽³⁾ reported that the low temperature martensite of Li has the hcp structure. The result, however, has been overthrown by the following neutron scattering studies. The neutron method is advantageous to the structural study of Li because the cross section of neutron scattering for ^7Li is much larger than that of X-ray scattering. McCarthy and others⁽³¹⁾ examined polycrystals of 99.99% pure ^7Li in a temperature range 4.2–300 K and showed that the structure of the low temperature martensite is not hcp but a complex structure with stacking faults. Later Overhauser⁽³²⁾ analysed their experimental results and proposed the martensite structure to be 9R. Smith⁽³³⁾ studied a single crystal of natural Li and found that MPT occurs partially and the low temperature martensite has the 9R structure with stacking faults. Since then many neutron scattering studies^{(34)–(37)} have confirmed this result.

The martensite structure and MPT of Li under pressure have been also examined by neutron scattering method. Smith and others⁽³⁸⁾ carried out high resolution neutron diffraction study in a temperature range 45–300 K under hydrostatic pressure 6.5 kbar, and found that MPT from bcc to 9R occurs partially at 90 K, and M_s rises under pressure. In contrast with this result, X-ray studies with diamond anvil⁽³⁹⁾⁽⁴⁰⁾ showed that the fcc martensite is formed under pressure. At present, the reason of disagreement between the results of X-ray and neutron diffraction is not clear. The rise of M_s under pressure is incompatible with that of pseudopotential calculation⁽⁴¹⁾⁽⁴²⁾, which predicts lowering of M_s of Li under pressure. Vaks and others⁽³⁵⁾ reexamined the band structure of Li by a pseudopotential method and proved that, since the Fermi level of Li moves towards the peak of density of electronic states with increasing pressure, *i.e.* due to the effect of proximity, M_s of Li rises under pressure.

Smith and others⁽³⁸⁾ also revealed that the low temperature 9R martensite changes to the fcc phase by heating to 140 K under hydrostatic pressure 6.5 kbar. Later they found the 9R to fcc MPT to occur by heating to about 90 K without loading⁽³⁷⁾. Schwarz and Blaschko⁽³⁶⁾ further showed by TOF (time of flight) neutron study on ^7Li single crystal that the fcc martensite always coexists with the 9R one below 80 K and, by heating above 80 K, the 9R to fcc MPT takes place. The results mentioned above would support that the low temperature martensite of Li has the 9R structure. However, since the martensite includes a large amount of stacking fault, its diffraction pattern becomes complicated, *e.g.* diffraction peaks shift with intensity modulation, which leads to ambiguities in the structure analysis. Any way, more structural study must be carried out in order to understand the nature of MPT

in Li.

Phonon dispersion relation of alkali metals was first measured by Woods and others⁽⁴³⁾ on Na in order to search the Kohn anomaly⁽²⁷⁾⁽²⁸⁾ found by Brockhouse and others⁽⁴⁴⁾ in Pb, which showed pronounced irregularities, *e.g.* kink at $q \approx 0.3q_0$ on the [110]LA branch. They could not find the Kohn anomaly in Na but observed low-lying [110]TA₁ branch. The phonon dispersion relation of the bcc-Li metal was first measured at 98 K by Smith and others⁽⁴⁵⁾ and calculated by Ono⁽⁴⁶⁾. Later Beg and Nielsen⁽⁴⁷⁾ was also examined the dispersion curves of Li in a temperature range 110–424 K. All the results obtained are well compatible with each other and also with the result of Na. The [110]TA₁ branch of Li is considerably low-lying but the Kohn anomaly is not found also in this case.

It is reported that the [110]TA₁ phonon branch of the bcc-Li metal exhibits anomalous temperature dependence. Ernst and others⁽⁴⁸⁾ studied the [110]TA₁ branch in a wide range of temperature and observed *en bloc* fall of phonon energies with lowering temperature towards M_s ; a marked fall took place near $4/5q_0$. According to Smith⁽³³⁾, however, the dispersion curve exhibits only a slight decrease (about 10%) at the Brillouin zone boundary (N-point) near M_s , but the amount of lowering falls off with approaching the zone center (Γ -point), where phonon energies rather increase by cooling. Later, Schwarz and others⁽²⁶⁾⁽²⁷⁾ have confirmed a slight softening at the N-point and also found a small dip near $q = 2/3q_0$.

Since the gradient of the [110]TA₁ phonon dispersion curve at the Γ point corresponds to the shear constant C' , the result by Ernst and others⁽⁴⁸⁾ should lead an opposite inference on the lattice instability from that by Smith⁽³³⁾: the former is affirmative to the Zener mechanism while the latter is negative. On the other hand, Felice and others⁽⁴⁹⁾ measured the elastic constants of Li by ultrasonic pulse-echo method and revealed that the elastic behaviours of C_L , C_{44} and C' are normal in a temperature range between 90 and 300 K. That is, all elastic constants increased by cooling. A theoretical calculation⁽⁵⁰⁾, based on the pseudopotential method also showed that the elastic constant C' of Li behaves normal temperature dependence. Although the reason of the above confliction is not clear, but the results of Smith⁽³³⁾ would be reliable because the elastic constants can be more precisely determined by ultrasonic pulse-echo method than by the phonon dispersion curves.

These situations suggest that a short wave-length phenomenon, other than the long wave-length limit, would relate to the lattice instability of Li. Since the modulation from bcc to 9R needs a wave with $q = 2/3[110]q_0$, we could expect an indication related to such a wave to appear near $2/3q_0$ on the [110] TA₁ phonon branch. Ernst and others⁽⁴⁸⁾ and Schwartz and others⁽⁵¹⁾⁽⁵²⁾ indeed found a slight dip near $2/3q_0$ on the [110]TA₁ branch by cooling to 78 K. However, Smith⁽³³⁾⁽⁴⁵⁾ could not find such an anomaly and, as noted by Shapiro⁽⁵³⁾, the dip is not significant if we take error

bars into consideration. In addition, it would be appropriate to interpret^{(48)–(50)} that the anomaly is due to an interaction of the $[110]TA_1$ phonon mode with defects such as nuclei of low temperature phase. On the other hand, the $[110]TA_1$ branch exhibits an evident softening at the zone boundary by cooling, although it does not reach to zero frequency but only about 10% decrease at most. However, it must be emphasized that the corresponding wave vector, $q=q_0$, is responsible to a lattice modulation from bcc to 2H. It has no relation with the 9R lattice formation.

The above mentioned results reveal clearly that the $[110]TA_1$ phonon dispersion relation in the bcc-Li metal does not exhibit any precursor phenomenon associated with MPT to 9R. Neither C' -softening nor soft phonon mode has been found even when cooled just above M_s . Concerning MPT of Li, on the other hand, Gooding and Krumhansl⁽⁵⁴⁾ proposed along the Landau theory that MPT takes place via incomplete softening near $2/3q_0$ of the $[110]TA_1$ dispersion relation due to strong anharmonicity. It is clear, however, that this proposal is not valid to MPT in Li because of lack of such a softening. Recently, Krumhansl⁽⁵⁵⁾ has illustrated that any softening of the $2/3[110]TA_1$ phonon is not necessary for the first order MPT. He proposed that not dynamic instability but thermodynamical anharmonicity is important for MPT. We also emphasize that, as well as the study of anharmonicity, a precise interplanar force constant analysis of the phonon dispersion relation is important to reveal the nature of MPT in Li. Details will be discussed later.

2. Na metal

Barrett⁽⁴⁾ found first MPT from bcc to hcp to occur partially (several percent) in Na by the X-ray diffraction study. Phonon dispersion relation of Na was first observed in 1962 by Woods and others⁽⁴³⁾ at 90 K. On the whole, the observed dispersion relations agree well with the theoretical ones obtained by Toya⁽⁵⁶⁾. Since then, several workers^{(57)–(59)} have examined lattice dynamical properties of Na as well as other alkali metals. Dolling and others⁽⁵⁷⁾, for example, measured phonon dispersion curves in order to search a soft-mode-like instability corresponding to cooperative atomic shear displacements for the bcc to hcp transformation. However, they could not find any anomaly: the dispersion curves exhibited only trivial temperature dependence. Neither $2/3q_0$ dip on the $[110]TA_1$ branch nor $2/3q_0$ anomaly on the $[112]TA$ branch has been observed: only the $[110]TA_1$ phonon branch showed a few percent softening at the zone boundary⁽⁶⁰⁾⁽⁶¹⁾.

Concerning MPT in Na, we have interest in pressure effect on the transformation temperature. As already mentioned, Vaks and others⁽³⁵⁾ observed that the gradient of M_s to pressure is positive for Li while negative for Na. Smith and others⁽⁶²⁾ performed neutron scattering experiments on MPT of polycrystalline Na under pressure and confirmed the negative gradient of M_s to pressure: they found decrease of M_s by 15 K with increasing

pressure of 1 kbar. This phenomenon can be explained by pseudopotential calculation⁽³⁵⁾ that, if there is no proximity effect of the Fermi level to the electronic energy density of states by pressure, M_s decreases by pressure as observed in Na.

Recent neutron scattering studies⁽⁶²⁾⁽⁶³⁾ show that the martensite of Na consists of both the 9R and hcp lattices within the bcc matrix. Relative volume fractions depend on temperature and specimen characteristics. Upon heating, the reverse transformation takes place at about 30 K, at which neutron scattering peaks of 9R begin to diminish. During further heating, the hcp intensities also decrease and, at 80 K, no traces of reflections of martensites are observed. Both 9R and hcp peaks were reported to be broadened and shifted from their ideal positions, which indicates a high stacking fault density.

Since Na is a typical simple metal, it is favourite to test the validity of pseudopotential theory. Such theoretical studies⁽⁶⁴⁾ have predicted appearance of the Kohn anomaly⁽²⁷⁾⁽²⁸⁾ on the phonon dispersion curves of Na. So far, however, any lattice dynamical studies on Na could not find the predicted anomaly. Concerning neutron elastic diffuse scattering, there is some controversial results. Blaschko and others⁽⁶¹⁾⁽⁶³⁾ observed a temperature dependent diffuse scattering above M_s , which was attributed to the formation of an intermediate defect structure. Similar phenomena were also observed by Ernst and others⁽⁴⁸⁾. These results, however, are contradicted by other workers⁽³⁷⁾⁽⁴⁵⁾⁽⁵⁸⁾⁽⁶⁰⁾, who did not observe any pre-transformation diffuse scattering. Berliner and others⁽⁶⁵⁾ recently measured in detail diffuse scattering, diffraction linewidth, quasielastic scattering and temperature dependence of the $[110]TA_1$ phonon energies above M_s . No evidence of transformation precursor was proved in their experiments. The ultrasonic study on Na⁽⁶⁶⁾ above M_s also could not prove the precursor effect.

3. K, Rb and Cs metals

Previously, Overhauser⁽⁶⁷⁾ has suggested a possibility of phase transition occurring with the CDW instability. In order to search CDW in the bcc K metal, Giebutowicz and others⁽⁶⁸⁾ performed neutron scattering experiments and found satellite peaks due to CDW. According to Pintschovious and others⁽⁶⁹⁾, however, the satellites were not due to CDW but double reflections: the result was also supported by X-ray study⁽⁷⁰⁾.

Dagens and others⁽⁷¹⁾ calculated the phonon dispersion relations of the bcc K metal and predicted the existence of a significant anomaly on the $[110]TA_1$ phonon branch. Such a prediction, however, is not compatible with the results of previous theoretical studies⁽⁷²⁾. Dolling and Meyer⁽⁷³⁾ examined experimentally the $[110]TA_1$ phonon branch of the bcc K metal at 4.3 K, but they could not find any trace of the anomaly predicted theoretically. At the present stage, this disagreement seems to be entirely due to computational problem. Blaschko and others⁽⁷⁴⁾ measured temperature dependence of the $[110]TA_1$ phonon branch of K down to 4 K, and reported a slight decrease of phonon energy at the zone boundary to occur

below 100 K, which would indicate a possibility of transformation induced by the zone boundary instability. They also examined neutron elastic diffuse scatterings near the 110 and 220 Bragg peaks and found the Huang scattering which increases below 70 K. They supposed that the scattering is induced by the formation of interstitial defects. Berliner and others⁽⁷⁵⁾ performed neutron powder diffraction to search a phase change, but any evidence of transformation was not observed even at 10 K. According to neutron scattering study by Werner and others⁽⁷⁶⁾, on the other hand, diffuse maxima were observed near the 110 and 220 Bragg peaks. Such maxima, however, are well explained as double scattering peaks⁽⁷⁷⁾. In conclusion, the bcc K metal exhibits neither transformation behaviour nor premartensitic anomaly.

Copley and Brockhous⁽⁷⁸⁾ measured several phonon branches of the bcc Rb metal at 12, 85, 120 and 250 K, but they did not find any pronounced temperature change in each branch. The Cs metal crystallizes into the bcc structure just above room temperature, but the bcc Cs metal does not undergo MPT by cooling: only the transformation from bcc to fcc is known to occur under the pressure of about 34 kbar. Ross and McMahan⁽⁷⁹⁾ suggested that such a MPT would be originated from a pressure induced s-d electronic transition. So far, lattice dynamical study on the bcc Cs metal has been carried out only by Mizuki and Stassis⁽⁸⁰⁾ but any anomaly has not been observed in connection with the premartensitic phenomenon.

III. Group-IV Metals

The group-IV metals Ti, Zr and Hf with the bcc structure transform in common to the hcp martensite by cooling to 1156, 1135 and 2015 K respectively. Both the bcc and hcp phases transform furthermore to the ω -phase under pressure. Concerning the bcc to ω transformation, we must refer to the Zr-Nb alloy. It exhibits remarkable anomalies such as structural fluctuation, phonon anomaly and others prior to the transformation⁽⁸¹⁾. However, there are not so much studies on the bcc phase of the group-IV metals, because they exist respectively in very high temperature regions. Lattice dynamical study by neutron inelastic scattering has so far been performed by two groups as described in the following.

Stassis and others⁽⁸²⁾ prepared a bcc single crystal Zr by repeating heat and cool through the M_s temperature and then holding at 1400 K. They measured the [001], [110] and [111] phonon dispersion curves at 1400 K and found a deep valley at $2/3q_0$ on the [111]LA branch. They argued that the anomaly would be a precursor of the bcc to ω transformation. It is also reported that both the [110]TA₁ and the [110]TA₂ branches degenerate each other, although such a degeneracy was corrected later by their own neutron scattering study⁽⁸³⁾. They found the low-lying [110]TA₁ branch and explained it to be instability phenomenon of the bcc phase.

On the other hand, the group-IV metals are well known as materials with anomalously fast self-diffusion.

The diffusivities of them at melting temperature are several orders of magnitude higher than for other bcc metals. Self diffusion behaviours can be examined by using quasielastic neutron scattering method⁽⁸⁴⁾ which is advantageous to direct determination of diffusion jump frequency. That is, we can obtain the jump frequency from the following equation by analysing the full line width at half-maximum (FWHM) of incoherent neutron scattering peaks due to diffusing atoms.

$$\Gamma = (2\hbar/\tau)[1 - \sin(Qd)/Qd]f, \quad (1)$$

where Γ is FWHM, $1/\tau$ the jump frequency, Q the wave vector, d the jump distance, and f the correlation factor. This method was used by several workers^{(85)–(87)} in order to analyse the self diffusion in the bcc Ti, Zr and Hf metals.

Petry and others⁽⁸⁸⁾ found anomalous phonon behaviour in the bcc Ti metal in the course of self-diffusion study by neutron scattering method. In order to study the bcc Ti metal, they developed a floating zone furnace⁽⁸⁹⁾ to grow single crystal at high temperature *in situ* on a neutron spectrometer. One of the essential ideas of this furnace is crucible-free growth of single crystal. To reduce the background of neutron scatterings, heating was achieved by sending a current directly through the specimen. The inelastic scattering experiments at 1293 K revealed a deep valley to appear at $2/3q_0$ on the [111]LA branch. The valley reaches down to zero energy at which no coherent elastic scattering is observed. An extraordinary low frequency at the zone boundary on the [110]TA₁ branch was also found by their experiments. They concluded that phonon behaviours with aforementioned characteristics act as a trigger to the elementary jump for self diffusion.

Meanwhile theoretical studies on the dynamics of MPT in these metals have been carried out through the first principle total energy calculation^{(90)–(92)}. The theories predict the existence of particularly low-energy phonons

Fig. 1 Phonon dispersion relations of the bcc Ti metal at 1293 K (The [110]TA₁ branch is measured at 1238 K). The solid line shows a Born-von Karman fit with force constants up to the fifth nearest-neighbour atoms. By W. Petry and others⁽⁹³⁾.

as precursor: the phonons become further soften when cooled near M_s . Under such a situation, Heiming and others⁽⁹³⁾ examined in detail temperature dependence of the phonon dispersion of the bcc Zr metal. They observed that phonons at $2/3q_0$ on the $[111]LA$ branch are strongly damped and the $[110]TA_1$ branch falls down at q_0 during cooling in the bcc phase, although the softening is incomplete. They interpreted such anomalies as precursor fluctuations: the former is represented to the bcc to ω transformation and the latter to the bcc to hcp transformation.

Recently Petry and others^{(94)–(98)} examined further the phonon dispersion of the group-IV metals over the respective bcc phase regions. They revealed that the phonon behaviours of *in situ* grown bcc specimens resembles very much to each other and exhibit several remarkable characteristics. As shown in Fig. 1, the dispersion curves are dominated by some unusual phenomena as follows[†]:

(1) At $2/3[111]q_0$, the $[111]LA$ branch shows a pronounced dip and phonon intensity of Ti and Zr falls continuously down to zero energy transfer.

(2) The $[110]TA_1$ branch is throughout low-lying and shows a dip at the zone boundary.

Since the atomic displacements corresponding to the $2/3[111]LA$ phonon of the bcc lattice are just equivalent to those necessary for the bcc to ω transformation, Petry and others proposed that such a low-lying and temperature dependent phonon is a precursor fluctuation of the ω -formation in the bcc phase. From the experimental fact that the $2/3[111]LA$ phonons of the group-IV metals do not change over the respective bcc phase regions, they concluded that the weakness towards ω fluctuation is an intrinsic bcc property. They also maintained that the low energy $[110]TA_1$ phonon at the zone boundary is related to the bcc to hcp transformation as precursor instability. We must notice, however, that the softening of the zone boundary phonon is incomplete even when cooled near to M_s , and hence we cannot accept the soft phonon schema as the mechanism of the bcc to hcp MPT in the group-IV metals.

IV. β -Phase Alloys

Lattice dynamical properties of the β -phase alloys are located at between A-15 compounds and alkali metals. The A-15 compounds with the β -W type structure transform with nearly second order characteristics to a tetragonal phase by cooling. Above the transformation temperature, the compounds exhibit almost complete softening of the elastic constant $C'_{(18)(99)(100)}$, and simultaneously soft phonon mode of the $[110]TA_1$ dispersion curve at the Γ -point⁽²⁵⁾⁽¹⁰¹⁾. The anomalies can be successfully explained within the framework of Landau theory⁽¹⁰²⁾. However, as mentioned in the section II, no softening has been found in the alkali metals in relation

to MPT. The β -phase alloys, on the other hand, are characterized by incomplete softening. As already described, the β_1 phases of Cu–Zn⁽⁵⁾⁽⁶⁾ and AuCd⁽⁷⁾ alloys have anomalously high elastic anisotropy, $A = C_{44}/C'$, which increases with decreasing temperature.

Gilat and Dolling⁽¹⁰³⁾ examined the phonon dispersion relation of β brass (mainly Cu–47 at%Zn alloy^{††}) with the B2 structure by inelastic neutron scattering method. Their interest, however, was only concerned with lattice dynamics related to the order-disorder transformation at 727 K. Studies on the phonon dispersion relations in connection with MPT were first due to Hoshino and others⁽¹⁰⁴⁾ for Cu–Al–Ni alloy and by Mori and others⁽²⁶⁾ for AuCuZn₂. The former study performed phonon measurements of the β_1 phase of a Cu–26Al–4Ni alloy at 293 K: no anomaly was observed in any phonon branch except the lowlying $[110]TA_1$ mode. On the other hand, the phonon dispersion obtained by the latter study for AuCuZn₂ exhibits an anomalous phenomenon.

As shown in Fig. 2, the $[110]TA_1$ branch of the β_1 -AuCuZn₂ alloy shows a softening near $2/3q_0$ with lowering temperature towards M_s , which gives rise to a dip on the dispersion curve. The shift of frequency, however, is at most 25% of the value at 567 K: the frequency remains finite even at M_s . That is, the softening is only partially attained when MPT takes place. Therefore, MPT in AuCuZn₂ does not relate directly to the dynamical instability or the soft phonon mode. The slope of the $[110]TA_1$ branch at the Γ -point corresponds well to the shear constant C' obtained by Nakanishi and others⁽⁸⁾. Mori and others also found elastic satellite reflections corresponding to the $2/3q_0$ dip. They supposed that the Fermi surface would have a flat section at $(2/3, 2/3, 1/2)$ in the reciprocal lattice, and that the $2/3q_0$ dip and corresponding satellite reflections may be attributed to the Kohn anomaly⁽²⁷⁾⁽²⁸⁾.

Guenin and others⁽¹⁰⁵⁾ studied the β_1 -Cu–19.3Zn–13.0Al alloy by neutron scattering experiments: the alloy transforms to the 18R martensite at 270 K. They found that the $[110]TA_1$ branch is very low-lying and shows the $2/3q_0$ dip. Whole branch decreased in energy with decreasing temperature whereas the dip did not change significantly. Elastic peaks were observed at $1/3q_0$, not at $2/3q_0$ as was the case of AuCuZn₂. They found that the shear constant C' deduced from the phonon dispersion curve was 20% higher than that obtained by ultrasonic method⁽¹¹⁾. They also examined the β_1 -Cu–7.2Zn–23.1Al alloy undergoing the transformation to the 2H martensite at 250 K⁽¹⁰⁶⁾. It is remarkable that there is no essential difference between characteristics of the $[110]TA_1$ branches of these two Cu–Zn–Al alloys. That is, the $[110]TA_1$ branches of them exhibit similar temperature change and also have the $2/3q_0$ dip in common, although both alloys undergo different type of martensite each other. These results suggest that the $2/3q_0$ dip has no relation with the 18R (or 9R) martensite.

Abbe and others⁽¹⁰⁷⁾ performed neutron inelastic scat-

[†] In the present overview, we use eV unit to express phonon energy for convenience ($\text{eV} = 1.602 \times 10^{-19} \text{ J}$).

^{††} The alloy composition is of atomic unit in the present overview.

Fig. 2 Temperature dependence of the [110]TA₁ phonon branch of the Heusler type AuCuZn₂ alloy above M_s . By M. Mori and others⁽²⁶⁾.

tering studies, as well as specific heat and susceptibility measurements, of several kinds of Cu-Zn-Al alloys, quenched from 1120 K, with M_s near 0 K. The neutron studies show that the [110]TA₁ branch is not altered appreciably when temperature varies from 6 to 215 K. Based on the specific heat measurements, they concluded that the electron-phonon interaction is not important but phonon specific heat is anomalously large due to small C' .

Concerning MPT, Kelly and Stobbs⁽¹⁰⁸⁾ studied the β -phase alloys along the Landau theory and proposed a soft-mode instability towards the β_1 to ω type lattice modulation caused by a coupling between the [111] CDW and the corresponding [111]LA phonon branch. This proposal is based on an analogy to the situation of the β_1 -CuZn alloy⁽¹⁰⁹⁾ where the Fermi surface has considerably flat faces perpendicular to the [111] direction, and such a nesting set up CDW. They also proposed a minimum at $2/3q_0$ along the [111]LA branch on the dispersion surface to appear. In order to verify their proposal, Robinson and others⁽¹¹⁰⁾ carried out a neutron scattering study on the quenched β_1 -AuCuZn₂ alloy. The phonon measurements, however, proved that there is no soft-mode behaviour in the [111]LA branch. This means that the theory of Kelly and Stobbs can not be applied to the β -phase alloys in general. Robinson and others also found anomalous elastic scatterings at $1/3[110]q_0$ and $[110]q_0$ along the [110] axis, in addition to the $2/3[110]q_0$ peak found by Mori and others⁽²⁶⁾, and ω -like peak along the [111] axis. The $1/3q_0$ and $2/3q_0$ peaks disappear by heating but the q_0 peak still remains: the ω -like peak disappears at 423 K and is never reproduced again by

cooling. The origin of these anomalies, however, is not clear at this stage.

The [110]TA₁ phonon dispersion of the β_1 -Cu-Al-Ni alloy was again examined by Morii and Iizumi⁽²⁹⁾. They observed anomalous dip around $2/3q_0$: the result disagrees with that reported by Hoshino and others⁽¹⁰⁴⁾. Morii and Iizumi examined the dispersion surface around the [110]TA₁ branch and found the phonon energies increase sharply as the q -position departs from the [110] axis. That is, the dispersion surface near the [110]TA₁ branch forms a steep valley along the [110] axis. The [110]TA₁ phonon branch is low-lying and it is slightly enhanced by cooling to M_s . Such a softening, however, is too weak and incomplete to regard it as the origin of MPT. The shear constant C' calculated from the slope of the dispersion curve at the Γ -point is in good agreement with that obtained by ultrasonic pulse echo method⁽⁹⁾.

They carried out further the interplanar force constant analysis of the observed [110]TA₁ branch. The analysis is based on the fact that the dispersion relation on the symmetry axes such as the [110] direction in the cubic lattice can be expressed by a linear chain model⁽¹¹¹⁾. In this model, particles constituting the chain represent atomic planes perpendicular to the chain, and interatomic forces are replaced by effective interplanar forces between the atomic planes. The dispersion relation is then expressed as

$$M\omega^2(q) = \sum \Phi_n [1 - \cos(n\pi q/q_0)], \quad (2)$$

where M is reduced atomic mass and Φ_n is the effective interplanar force constant between the n -th neighbour atomic planes. According to their analysis of the [110]TA₁ phonon branch of the β_1 -Cu-Al-Ni alloy, both Φ_2 and Φ_3 are positive and comparable. Based on this result, they concluded that the β_1 -Cu-Al-Ni alloy has dual lattice instability towards both the 2H and 18R martensites. Concerning this subject, we will discuss later in detail.

They also examined temperature dependence of elastic scattering intensity along the [110] axis and several off-axis directions. An anomalous peak was found above 332 K at the zone boundary of the [110] direction but it disappeared near M_s . This is contrary to the expectation that, if elastic scattering at the zone boundary would be a certain kind of precursor of the 2H martensite, it should increase as approaching M_s . Anomalous peaks also appeared at both $1/3q_0$ and $2/3q_0$, which exhibited a very complicated temperature dependence. The origin of these anomalous peaks remains unsolved. It is sure at least, however, that there is no one-to-one correspondence between the anomalous q_0 peak and the 2H martensite formation, or between the $2/3q_0$ peak and the 18R (or 9R) martensite formation.

The [110]TA₁ phonon dispersion relation of Cu-Al-Ni alloy was again measured by Hoshino and others⁽¹¹²⁾ in order to check the presence of phonon condensation concerned with the 2H martensite formation. The dispersion curve showed a slight decrease with decreasing tempera-

ture to M_s , but they could not find any anomaly such as the $2/3q_0$ dip as found by Morii and Iizumi⁽²⁹⁾. It is not clear at present whether this discrepancy is due to sample dependence or any other. Hoshino and others also examined the $[100]TA$ phonon branch of a single crystal of the 2H martensite: the branch corresponds to the $[110]TA_1$ branch of the β_1 phase. However, they could not observe any evidence for the soft mode, and hence they concluded that the presence of phonon instability is ruled out not only in the β_1 phase but also the 2H phase.

We studied several β_1 -AuCuZn₂ alloys by using neutron scattering method, and performed the interplanar force constant analysis on the obtained $[110]TA_1$ branches, with extending such a analysis to the other β_1 phases measured so far⁽¹¹³⁾⁽¹¹⁴⁾. The obtained force constants Φ_2 and Φ_3 are summarized in Table 1 as the ratios to Φ_1 . It is clear that materials are classified into three groups according to combination of Φ_2 and Φ_3 . We must notice that such groups have a one-to-one correspondence to those classified by structures of the martensite to be formed.

The TI metal transforms to the 2H (hcp in this case) martensite and belongs to the first group with $\Phi_2 > 0$ and $\Phi_3 < 0$ ⁽¹¹⁵⁾. This situation can be explained as follows. The large positive Φ_2 means that the (110) planes of the second nearest neighbours are coupled through a strong restoring force each other but, since Φ_3 is negative, there is no restoring force in between the third nearest neighbours. As a result, shuffling should occur with every two atomic planes and hence the 2H structure will be formed. If Φ_3 is positive as is the case of AuCuZn₂, on the other hand, the 9R (or 18R) lattice will be formed because the shuffling on every third (110) plane must occur. When both Φ_2 and Φ_3 are positive as is the case of the

group II, the formation of 2H and 9R (or 18R) lattices will compete with each other. In the case of the β_1 -Cu-Al-Ni alloy, for example, the 2H martensite is formed by cooling, while the 18R martensite is induced under the stress field⁽¹¹⁶⁾. Thus we can predict the martensite structures to be formed in the β_1 phases, if we have the force constants Φ_2 and Φ_3 .

As mentioned above, the $2/3q_0$ dip appears on the $[110]TA_1$ phonon dispersion curve of many β_1 phases. However, without doubt, such a dip is not an essential property belonging exclusively only to the β_1 phases which transform to the 9R (or 18R) martensite. That is, the $2/3$ dip does not correspond directly to the shuffling wave required to form the 9R (or 18R) lattice. From this viewpoint, an interplanar force constant analysis would be significant because the phonon dispersion curves can be expressed as a function of the interplanar force constants. Concerning this problem, we performed a computer simulation⁽¹¹⁷⁾ of the $[110]TA_1$ phonon dispersion curves along the interplanar force constant analysis using eq. (2). Figure 3 shows some examples of the phonon dispersion curves calculated with various combinations of Φ_2 and Φ_3 .

It is clear that the $[110]TA_1$ phonon branches accompanied by either $2/3q_0$ or q_0 dip observed so far can be satisfactorily reconstructed by using up to the third terms, with the coefficients Φ_1 , Φ_2 and Φ_3 , of the Fourier series in eq. (2). The cases of Ti⁽¹¹⁵⁾, Cu-Zn-Al⁽¹¹⁾, Cu-Al-Ni⁽²⁹⁾ and AuCuZn₂⁽²⁶⁾⁽¹¹³⁾⁽¹¹⁴⁾, for example, correspond approximately to the sets ($\Phi_2=0.9$, $\Phi_3=-0.3$), ($\Phi_2=0.2$, $\Phi_3=0.1$), ($\Phi_2=0.2$, $\Phi_3=0.2$) and ($\Phi_2=-0.3$, $\Phi_3=0.2$), respectively.

These results mean that both the $2/3q_0$ and q_0 dips appearing on the $[110]TA_1$ phonon dispersion curves are

Table 1 Interplanar force constants Φ_2 and Φ_3 , expressed as the ratios to Φ_1 , between the (110) planes of the β_1 phases and TI metal. They are obtained from analysis of the $[110]TA_1$ phonon dispersion relations. RT is room temperature, Q and S mean respectively the quenched and slowly cooled specimens.

Group	Material	Temp.	Φ_2	Φ_3	Marten	Ref.
I	TI	RT	0.89	-0.25	2H	(115)
II	Cu-47Zn	RT	0.07	0.06	2H, 18R	(103)
	Cu-25.4Al-5.4Ni	372 K	0.09	0.10	2H, 18R	(29)
		295	0.18	0.09		
	Cu-19.3Zn-13.0Al	RT	0.04	0.09	18R	(105)
	Cu-7.2Zn-23.1Al	RT	0.16	0.10	2H	(106)
III	Au-30Cu-47Zn	567 K	-0.11	0.08	18R	(26)
		516	-0.13	0.11		
		448	-0.15	0.11		
		298	-0.21	0.14		
	Au-30Cu-47Zn	RT	-0.09	0.10	18R	(110)
	Au-25Cu-50Zn(Q)	RT	-0.13	0.20	18R	(113)(114)
			-0.10	0.19		
	Au-26Cu-48Zn(Q)	(S)	-0.25	0.24		
			-0.10	0.16		
	Au-30Cu-48Zn(Q)	(S)	-0.07	0.07		
			-0.05	0.07		

simply due to characteristics of the Φ_2 - Φ_3 space. Slight fall of the dips with decreasing temperature observed in several alloys can be enough explained by a term of temperature dependent variation of Φ_2 and Φ_3 . In Table 1, we can see that Φ_2 of Cu-Al-Ni increases by cooling while Φ_3 is almost constant. Such characteristics would cause a structural instability of the β_1 phase towards the 2H lattice. The positive and constant Φ_3 over a wide range of temperature suggests that the β_1 phase could always transform to the 18R martensite, if the stress field is applied. In fact, this is the case of the β_1 -Cu-Al-Ni alloy⁽¹¹⁶⁾.

On the other hand, the quenched β_1 phases of CuZn⁽¹¹⁸⁾, NiAl⁽¹¹⁹⁾⁽¹²⁰⁾ and AuCuZn₂⁽¹¹⁰⁾ exhibit in common the ω -like peaks on the diffraction patterns. Such peaks appear at nearly the same positions as those of the superlattice reflections from the ω phase found in Ti- or Zr-alloys. According to de Fontain⁽¹²¹⁾, the ω phase results from lattice modulation by the $2/3[111]$ LA or equivalent $1/3[112]$ TA lattice wave. Indeed in the case of Zr-Nb alloy⁽⁸¹⁾, the $[111]$ LA and $[112]$ TA phonon dispersion relations exhibit anomalous valley in common. Therefore we can also expect a certain kind of precursor of the ω -formation in the β -phase alloys to appear. From this viewpoint, we investigated in detail the nature of the ω -like peaks observed in the quenched β_1 -AuCuZn₂ alloy by neutron scattering experiments⁽¹²²⁾.

The obtained results, however, prove evidently that the ω -like peak is neither due to the ω phase formation as is the case of Zr-Nb alloy nor precursor of MPT. Origin of the ω -like peak in the β_1 -AuCuZn₂ alloy relates essentially to regular arrangements of atomic vacancies in the incompletely ordered phase with the B2 structure existing stably above about 670 K. The regularity of vacancy arrangements is an inherent property of the incompletely ordered B2 phase undergoing the ordering to the Heusler structure. Such vacancies are frozen by quenching and hence the ω -like peaks are found in the quenched specimen at room temperature. During heating, however, the ω -like peak intensity disappears completely at about 600 K, at which quenched-in vacancies are annihilated⁽¹²³⁾, and then the peak begins to appear suddenly at about 670 K: the Heusler to B2 transformation occurs at that temperature. Figure 4 shows these situations.

It must be noticed that, when the quenched specimen is heated below 600 K and then cooled to room temperature, the ω -like peaks cannot be observed on the X-ray diffraction pattern, although they are found by a neutron scattering study. This phenomenon would be reasonable because the quenched-in vacancies in the specimen are annihilated from surfaces and X-ray can penetrate only several-ten μm of the specimen. The ω -like peaks produced in the B2 phase, however, disappears when the specimen is cooled very slowly to the Heusler phase region. These facts demand strongly that we must reexamine in detail the nature of anomalous scatterings observed so far in the premartensitic states in the β -phase alloys.

The $[111]$ LA phonon branch, on the other hand, has a deep valley at the ω -position, but the phonon energy on the $[112]$ TA branch at that point is maximum. That is, the phonon energy at the ω position of the $[111]$ LA branch is not minimum but a saddle value on the phonon energy surface. Therefore we can conclude that characteristics of these phonon branches have no relation to the ω phase formation⁽¹²²⁾.

Zolliker and others⁽¹²⁴⁾ carried out neutron scattering studies in order to search precursor effects in the β_1 -Cu-39.0Zn alloy with M_s at about 185 K. They found that the $[110]$ TA₁ branch is entirely low-lying than that of a stoichiometric CuZn⁽¹⁰³⁾ and becomes lower as approaching the M_s temperature. However, the temperature-dependent softening of such a low-lying mode does not exhibit any pronounced anomaly such as dip, nor is there a strong elastic scattering corresponding to the wave vector of stacking sequence of martensite. Only elastic diffuse streak is observed along the $\langle 110 \rangle$ direction, which highly correlates to a static atomic displacement.

Recently Planes and others⁽¹²⁵⁾ studied the ordered structures of the β_1 phases of Cu-14.5Zn-16.8Al ($M_s=255$ K) and Cu-18.9Zn-14.5Al ($M_s=168$ K) alloys by neutron scattering method, and determined the atomic positions of the Heusler (L2₁) structure. This method is more advantageous than X-ray or electron scattering method because the scattering lengths of Cu, Zn and Al for thermal neutrons are different enough from each other. They confirmed also that both the transformations of Heusler to B2 and B2 to bcc are second order.

We measured the $[110]$ TA₁ phonon dispersion relation of the β_1 -Cu₃Al(+Pd) alloy under the $[001]$ uniaxial pressure⁽¹²⁶⁾. The obtained results show that the phonon mode, which is low-lying as well as the other β -phase alloys, do not change so remarkably by the pressure: any anomaly such as dip is not induced. The interplanar force constant analysis indicates, however, that Φ_2 decreases with increasing pressure while Φ_3 increases. This means that the pressure enhances the instability towards the 18R martensite. The experiments by neutron elastic scattering revealed that the elastic peaks appear near the $2/3q_0$ positions along the $\langle 110 \rangle$ axes. Such peaks, however, could not be observed by the X-ray study. This situation suggests as is the case of the β_1 -AuCuZn₂ alloy that the anomalous scattering should be due to regularly distributed lattice defects, which are annihilated from surfaces.

As mentioned above, many β_1 phases exhibit several kinds of anomalies over a wide range of temperature above M_s . They appear in the form of a slight softening and $2/3$ dip of the $[110]$ TA₁ phonon dispersion, C' softening, diffuse scatterings at the ω - and/or $2/3[110]$ q_0 -positions, and others. It is clear, however, that MPT of the β phase alloys is first order. The softening of the $[110]$ TA₁ phonon dispersion relation, as well as C' softening, is indeed incomplete. Therefore, as argued by Krumhansl and Gooding⁽¹²⁷⁾, it is also evident that the soft mode theory cannot provide complete explanation of MPT. The $2/3q_0$ dip is not responsible to the 9R (or

Fig. 3 Series of the phonon dispersion relations calculated with various combinations of Φ_2 and Φ_3 . The cases of Tl, Cu-Zn-Al and AuCuZn₂ correspond respectively to the sets $(\Phi_2, \Phi_3) = (0.9, -0.3)$, $(0.2, 0.1)$ and $(-0.3, 0.2)^{(117)}$.

18R) martensite formation, because it appears even in the specimen which transforms to the 2H martensite. The anomalous elastic peaks have no relation to the martensite structure to be formed, but they would be probably due to lattice defects with regular arrangements. That is, precursor phenomena of the β phase alloys are not

remarkable. Also in the NMR experiments by Rubini and others⁽¹²⁸⁾, no precursor effects were observable above M_s . It must be emphasized, however, that we can find the direction of the β_1 -lattice-instability through the interplaner force constant analysis.

Fig. 3 (Cont.) Series of the phonon dispersion relations calculated with various combinations of Φ_2 and Φ_3 . The cases of Ti, Cu-Zn-Al and AuCuZn₂ correspond respectively to the sets $(\Phi_2, \Phi_3) = (0.9, -0.3)$, $(0.2, 0.1)$ and $(-0.3, 0.2)$ ⁽¹⁷⁾.

V. Ni-Base Alloys

1. NiTi alloy

The NiTi alloy is well known for its reversible shape

memory effect originating from MPT. In this alloy, MPT proceeds via a premartensitic transformation. That is, during cooling, the parent phase with the B2 structure undergoes a second-order like transformation to the intermediate phase, called the R-phase or premartensite

Fig. 4 The ω -like peak intensity near the position $(2/3, 2/3, 8/3)$ along the $[112]$ direction, obtained *in situ* neutron scattering experiments with increasing temperature⁽¹²²⁾.

phase, at T_c and then the martensite phase is formed at M_s by the first-order phase transformation. Bührer and others⁽¹²⁹⁾ have proved by a neutron diffraction study on the Ni-50.7Ti powder specimen at 10 K that the martensite has the monoclinic structure belonging to the space group $P2_1/m$: the R-factor of this structure analysis is 4.5%. The transformation temperatures are strongly composition dependent. Preceding MPT, the alloy exhibits anomalies of many physical properties such as electrical resistivity, sound velocity, internal friction, specific heat and others. The results obtained by extensive studies have been reviewed by Shabalovskaja⁽¹³⁰⁾.

Concerning dynamical properties of the premartensitic state, Moine and others⁽¹³¹⁾ studied the Ni-50Ti-3Fe alloy by inelastic neutron scattering. Substitution of Fe for Ni in NiTi expands the temperature range of the premartensitic state without structural change, which is advantageous to an extensive study of the B2 to R transformation and its precursor phenomena. They examined the $[100]$ and $[110]$ acoustic phonon branches in a temperature range between room temperature (RT) and 623 K, and temperature dependence of elastic neutron scatterings near the 210 Bragg peak. The results obtained reveal

a dramatical anomaly in the $[110]TA_1$ phonon branch. That is, as shown in Fig. 5, this branch exhibits an energy minimum near $2/3q_0$ which decreases rapidly towards zero energy with decreasing temperature. In addition, new superlattice peaks appear at RT near the $(5/3, 4/3, 0)$ type positions in the reciprocal lattice. It is initially incommensurate but becomes commensurate at low temperature. They conclude that the general features resemble very much low-dimensional systems where Fermi surface instabilities and the formation of CDW have been observed.

Independently of the work by Moine and others, Satija and others⁽¹³²⁾ have also studied the $[110]TA_1$ dispersion relation of the B2 phase of the Ni-50Ti-3.2Fe alloy in a wide range of temperature, and found a phonon softening near $2/3q_0$. They concluded that this phonon softening can be regarded as a Fermi surface-driven electron-phonon anomaly, and the premartensitic phase transformation is triggered by this soft phonon. Immediately after, Tietze and others⁽¹³³⁾ also carried out inelastic neutron scattering experiments on an equiatomic NiTi alloy. According to them, the $2/3q_0$ dip of the $[110]TA_1$ branch grows by cooling and arrives at zero energy at 338 K, while the $[111]LA$ mode exhibits a normal behaviour. These phonon behaviours do not agree with the prediction by Bruinsma⁽¹³⁴⁾. He calculated the contribution of electron-phonon interaction to the phonon dispersion relation of NiTi, and proposed that the anomalies associated with areas of the Fermi surface would appear on the dispersion curves. His calculation is based on the method developed by Varma and others⁽¹³⁵⁾. Elastic constants obtained from the initial slope of the phonon dispersion curves, on the other hand, agree well with those obtained by sound velocity measurements⁽¹³⁶⁾. It must be noticed that the elastic anisotropy factor is con-

Fig. 5 The $[110]TA_1$ phonon anomaly of NiTi at 293 K ($\bullet$), 356 K ($\times$), 423 K ($\circ$), 523 K ($\triangle$) and 623 K ($\square$). The arrows indicate the statistical error of the measurements at 293 K. By P. Moine and others⁽¹³¹⁾.

siderably smaller ($A \approx 2$) than that of the other shape memory alloys.

Tietze and others⁽¹³⁷⁾ performed also crystallographic studies on the equiatomic NiTi single crystal by neutron elastic scattering. Concerning the R phase formation at 348 K, they proved that the superlattice intensity is proportional to the reduced temperature $\tau = (T_c - T)/T_c$. That is, the B2 to R phase transformation is a second-order displacive transformation. They proposed that the R phase formation is driven by a condensation of the [110]TA₁ phonon mode, and the lattice distortion amplitude corresponds to the Landau order parameter with a critical exponent $\beta = 1/2$.

Condensation of the [110]TA₁ phonon mode near $2/3q_0$ has been indeed verified by neutron inelastic scattering study performed by Harget and others for an equiatomic NiTi and Ni-49.5Ti alloys⁽¹³⁸⁾⁽¹³⁹⁾. They also measured phonon density of states (PDOS) in martensite phase, R-phase and B2 phase of powder specimen by TOF method⁽¹⁴⁰⁾⁽¹⁴¹⁾. Within experimental accuracy, they could not find any significant difference of PDOS between the R- and B2-phases. In order to interpret these results, Keil and others⁽¹⁴²⁾ studied theoretically lattice dynamics by means of the model of Verma and Weber⁽¹³⁵⁾. Concerning the phase transformation, the result predicts the condensed [110]TA₁ soft mode near $2/3q_0$ due to the electron phonon interaction, and thus the transition to the R phase is caused by a strong coupling of specific electrons near the Fermi energy. We would approve that the B2 to R transformation of second order is accompanied by soft mode behaviour near $2/3q_0$ of the [110]TA₁ branch.

Zao and others⁽¹⁴³⁾ carried out a new self-consistent band structure calculation and obtained the electron-phonon matrix elements and phonon dispersion curves. According to them, the Fermi surface has a nesting feature and consequently the [110]TA₁ branch is drastically lowered towards zero energy at $2/3q_0$. They concluded that the B2 to R phase transformation is triggered by the nesting and resulting dip of the [110]TA₁ branch. A general lowering of this phonon branch contributes to push the $2/3q_0$ phonon to lower energy.

Kuentzler⁽¹⁴⁴⁾ performed specific heat measurements on the NiTi alloys with near-equiatomic compositions. At low temperature, the specific heat C is expressed as

$$C/T = \gamma + \beta T^2, \quad (3)$$

where γ and β are respectively electronic coefficient proportional to the density of states at the Fermi level and lattice coefficient related to Debye temperature θ_D . He found the maximum γ and the minimum θ_D to appear at the composition of 51.5 %Ni, at which M_s becomes minimum. Based on these results, he asserted the existence of nestings on the Fermi surface.

The studies mentioned above reveal that the R-phase formation in NiTi results from unique characteristics of its Fermi surface: a similar situation cannot be expected for the other alloys. Concerning the nature of the R phase, X-ray scattering study on the B2 phase of NiTi

(+Fe) by Shapiro and others⁽¹⁴⁵⁾ is also worth notice. They found anomalous shift of the superlattice reflections from the commensurate positions: incommensurability changes from Brillouin zone to Brillouin zone. The anomaly cannot be explained by such models as CDW and lattice distortion wave. As an explanation of this anomaly, Yamada⁽¹⁴⁶⁾ proposed a modulated lattice relaxation model which assumes existence of both a $2/3q_0$ dip on the [110]TA₁ phonon dispersion curve and embryos of low temperature phase. According to him, the size of embryos expands to the order of 10 nm. Since this size is larger enough than the resolving power of usual electron microscopy, such embryos should be observed experimentally if they exist.

2. NiAl alloy

In NiAl alloy system, the β_1 phase with the B2 structure appears in a wide range of compositions, i.e. 38–68% Ni, when the β phase is quenched. It is known that the B2 phase existing in about 60–68% Ni range undergoes MPT during cooling: M_s is extremely sensitive to alloy composition⁽¹⁴⁷⁾⁽¹⁴⁸⁾. The structure of martensite is also composition dependent. Alloys with composition less than about 63% Ni transform to the 7R-martensite while the Ni-rich alloys to the 3R- (L1₀ type) martensite^{(149)–(151)}. So far, however, premartensitic behaviours have been studied mainly for the alloys undergoing MPT to 7R.

The β_1 -Ni-36.8Al alloy exhibits a considerable softening of the shear constant C' with decreasing temperature towards M_s ⁽¹⁵²⁾. It is only lately, however, that the lattice dynamical studies on the β_1 -NiAl alloy have been performed with respect to the lattice instability prior to MPT. Shapiro and others⁽¹⁵³⁾ studied several β_1 -Ni_xAl_{1-x} alloys with $0.5 < x < 0.65$ by neutron scattering experiments. They found a pronounced dip to appear near $1/6[110]q_0$ on the [110]TA₁ phonon dispersion curve. The dip position is composition dependent, although phonon energy at the dip does not change appreciably with temperature. They also found elastic peaks at the positions near $1/6[110]q_0$, and they proposed that the elastic anomaly arises from the local accommodation of the structure to singular terms in the electron energy near $2k_F$, where k_F is the Fermi wave vector. As a common origin of these anomalies, and also of tweed contrast in electron microscopy, they proposed a mechanism concerning the electronic structure.

Shapiro and others⁽¹⁵⁴⁾⁽¹⁵⁵⁾ examined further the β_1 -Ni-37.5Al alloy by neutron scattering method and revealed that, with decreasing temperature towards M_s , the dip near $1/6q_0$ on the [110]TA₁ branch falls down, and simultaneously elastic scatterings develop at the same position in the reciprocal lattice. They also found in the 7R phase that superlattice reflections along the c^* direction, corresponding to the β_1 [110] direction, have a nonuniform spacing and unusual line shape, and regarded these anomalies to be due to stacking faults. Gooding and Krumhansl⁽¹⁵⁶⁾ have interpreted these anomalies as precursors of MPT resulting from phonon-

strain interaction.

Later Noda and others⁽¹⁵⁷⁾⁽¹⁵⁸⁾ studied again the 7R phase of Ni-37.5Al by neutron scattering method, and concluded that the 7R martensite consists of two kinds of seven-layered monoclinic cells with slightly different monoclinic angles. Concerning the 7R martensite, Yamada and others⁽¹⁵⁹⁾ developed theoretical treatments for atomic fluctuations in a highly anharmonic lattice by introducing a pseudospin variable, and discussed MPT as the ordering process of the pseudospins. They proposed that the order parameter takes on two different values alternatively in space. According to high-resolution electron microscopic studies on the β_1 -Ni-37.5Al alloy by Schryvers and others⁽¹⁶⁰⁾⁽¹⁶¹⁾, the premartensitic state includes a fine-scale mosaic assembly of nonuniformly distorted and modulated domains with the (110)[$\bar{1}\bar{1}$ 0] type shear and shuffle displacements. They considered that such displacements are derived from unusual behaviour of the [110]TA₁ phonon branch and the domains are the precursor to nucleation of the 7R martensite.

Hallman and Svensson⁽¹⁶²⁾ performed neutron scattering studies on the β_1 -Ni-50Al and β_1 -Ni-42Al alloys and observed similar anomalies to those reported by Shapiro and others mentioned above. They carried out the fifth neighbour Born-von Karman fits to the observed phonon dispersion curves and found that the force system of the alloys is dominated by the first and second nearest neighbour interactions. The second nearest neighbour force constants change as much as about 30% between both alloys, which is consistent with the theoretical assumption proposed by Clapp and others⁽¹⁶³⁾ in modelling MPT using molecular dynamics. Position of the elastic satellite peaks observed by them, however, are different from those predicted by Gooding and Krumhansl⁽¹⁵⁶⁾.

Recently Shapiro and others⁽¹⁶⁴⁾ performed inelastic and elastic neutron scattering studies in detail on the β_1 -Ni_xAl_{1-x} alloys for $x=0.5, 0.58, 0.625$ and 0.639% , and showed that the [110]TA₁ branch behaves very sensitively to alloy composition, so is the dip position in the q -space. They also found an incomplete softening in the vicinity of the dip of such a phonon branch with decreasing temperature towards M_s and, as shown in Fig. 6, under uniaxial pressure. The softening under uniaxial stress was interpreted in terms of Clapp's localized soft mode theory⁽¹⁶⁵⁾. The corresponding elastic diffuse anomalies increase in a similar fashion to the phonon softening.

Concerning the equiatomic NiAl alloy, studies by Mostoller and others⁽¹⁶⁶⁾ would be worth to refer from a viewpoint of the surface problem associated with MPT. They measured bulk and surface vibrational modes in NiAl by neutron inelastic scattering and electron energy-loss experiments, and found surface dipole-active vibrational modes occurring in the gap between the bulk acoustic and optical modes for the (110) and (111) surfaces. They conclude that, based on their calculation, the atomic motion for the gap modes is correlated with the bulk properties. This study has no concern directly with

Fig. 6 Effect of the [001] uniaxial pressure on the [110]TA₁ phonon branch of Ni-37.5Al alloy. By S. M. Shapiro and others⁽¹⁶⁴⁾.

MPT, but, in order to understand the lattice instability mechanism towards MPT, we would need to examine the surface vibrational modes in detail.

One of the most remarkable phenomena in the premartensitic B2 phase of NiAl is the $1/6q_0$ dip on the [110]TA₁ phonon dispersion relation. As proved in our previous study⁽¹¹⁷⁾, the $2/3q_0$ and q_0 dips observed on the [110]TA₁ phonon dispersion relation of the β -phase alloys can be reproduced by an appropriate combination of Φ_2 and Φ_3 which are the interplanar force constants between the second and third nearest neighbour (110) planes. The dip in the present case, however, cannot be simulated by the interplanar force constant method⁽¹⁶⁷⁾. Concerning the dip, Zhao and Harmon⁽¹⁶⁸⁾ studied theoretically the electronic band structure of the β_1 -NiAl alloy by using a linear combination of atomic orbitals method, and predicted that the $1/6q_0$ dip can be attributed to both strong electron-phonon interactions and Fermi surface nesting. The composition dependence of the dip-position was also predicted by their calculation. This situation indicates the necessity of experimental studies on the energy band structure of the B2 phase.

It must be noticed that, according to the NMR study on the B2 phase⁽¹⁶⁹⁾, tweed patterns observed by electron microscopic studies do not represent the nucleation of martensitic embryos. In addition, Chandrasekaran and others⁽¹⁷⁰⁾ have some questions about the martensite structure and structural precursors in the β_1 -NiAl alloy. Based on their electron diffraction and electron microscopic studies, they argued that the martensite structure reported as 7R could be explained as twinned 3R structure, and that stress effect and surface transformation could produce structural anomalies. Although electron diffraction or microscopic studies give only some par-

ticular information on materials, *i.e.* properties of thin film or surface, it needs to reexamine the martensite structure in detail in order to understand the nature of the B2 phase of NiAl.

VI. Other Metals

Although MPT of the In-Tl alloy does not belong to the subject of the present overview, it is worth notice from lattice dynamical viewpoint. The alloy with the fcc structure in a wide composition range, 15.5–31.0%Tl, undergoes MPT to a bct structure by cooling. For example, the shear constant C' tends to zero as the transition temperature is approached either by cooling of the fcc phase or by heating of the bct phase⁽¹⁷¹⁾⁽¹⁷²⁾. Therefore we can expect a soft mode at the Γ -point of the $[110]TA_1$ phonon branch. However, no experiment has proved any soft mode in MPT in the alloy⁽¹⁷³⁾⁽¹⁷⁴⁾. C' obtained from the initial slope of the $[110]TA_1$ branch is much larger than that obtained by ultrasonic measurements and, in addition, the small- q $[110]TA_1$ phonons perform normal behaviour, *i.e.* hardening as temperature approaches to M_s . At present, we cannot explain satisfactorily the discrepancy between neutron and ultrasonic data. As for details of dynamical behaviours in the premartensitic state, refer the literatures^{(171)–(174)}. In this section, we will consider the problems on the bcc-metals Tl Sc and La.

1. Tl metal

The bcc Tl metal would be unstable according to Zener's criterion⁽¹⁾ that the bcc structure cannot be stable, if the crystal consists of metal ions with completely filled innershells and the non-coulombic interaction between the closed shells is not negligible. Indeed the bcc to hcp transformation takes place in Tl at 503 K. Since the transformation temperature is relatively low, it might be expected that a considerable softening of the phonon dispersion relation of Tl would be observed near M_s . From this viewpoint, Worlton and Schmunk⁽¹⁷⁵⁾ measured phonon energies by neutron inelastic scattering along the $[100]$ and $[110]$ directions of a single crystal of the hcp-Tl metal at 77 and 296 K, but they could not find any anomaly attributable to the lattice instability.

The phonon dispersion relation of the bcc-Tl metal was first measured by Iizumi⁽¹¹⁵⁾ with purpose to examine the lattice instability associated with the bcc to hcp transition. He grew and kept a single crystal of the bcc-Tl metal within an electric furnace installed on the neutron-goniometer. The phonon energies were measured at 523 K for the as-grown specimen in the furnace along the $[100]$, $[110]$ and $[111]$ directions. It is remarkable that the $[110]TA_1$ branch is low-lying as a whole and exhibits an anomalous lowering of energy near the zone boundary (N-point). If the zone boundary phonon is responsible to the lattice instability of the bcc-Tl metal, it would suggest the formation of a hcp lattice at MPT since the wave vector at the N-point corresponds to that of lattice wave of the bcc to hcp modulation.

As already mentioned, phonons propagating along

high-symmetry directions in a simple lattice such as bcc can be analysed by a linear chain model⁽¹¹¹⁾. The analysis gives interplaner force constants for the particular types of vibrations. The results obtained by Iizumi are shown in Table 1. It is clear that Φ_2 , the interplaner force constant between the second nearest neighbour planes, is markedly large while Φ_3 is negative. This result indicates that there is a very strong restoring force between the second nearest neighbour planes which causes easiness of the shuffling towards the formation of the hcp-type structure. Such a conclusion consists with the real transformation schema of the bcc-Tl metal. The microscopic origin of the lattice instability of bcc Tl, however, has not been explained satisfactorily at the present stage.

2. Group-III metals

As mentioned in section II, Petry group^{(95)–(98)} have studied extensively lattice dynamical properties of the bcc phase of the group IV metals Ti, Zr and Hf which exhibit dynamical fluctuations indicating the ω -phase formation. On the other hand, the group III transition metals have only one d-electron and hence it is expected to be the “weakest” bcc metals. The bcc Sc metal, for example, transforms to hcp at 1610 K but no ω -phase is found, although the group IV metals transform to the ω -phase under pressure as well as to the hcp martensite by cooling. Under these situations, we are interested in the dynamical behaviour in the bcc Sc metal.

Since M_s of the bcc Sc metal is too high, Trappemau and others⁽¹⁷⁶⁾ have grown its single crystal in the furnace installed on the neutron-goniometer, as is the case of the group IV metals, and subsequently, without cooling the specimen below M_s , performed *in situ* phonon measurements at 1673 K along the $[100]$, $[110]$, $[111]$ and $[112]$ directions. The dispersion curves obtained resemble very much those of the group IV metals. That is, remarkable features are that the $[111]LA$ branch has a deep valley at $2/3q_0$, and the $[110]TA_1$ branch is low-lying.

All the low energy phonons are strongly broadened and overdamped and, due to overdamped phonons, inelastic scattering intensities reach down to zero energy transfer. A valley of low energy phonons extends along the Brillouin zone boundary in the $[112]$ direction. The authors have proposed that, as is the case of the group IV metals, these anomalies represent dynamical precursor fluctuations and, besides the bcc to hcp transformation, an ω modification would take place under pressure: the eigenvectors of these anomalous modes correspond to the displacements required for the formation of both the hcp and ω lattices.

The bcc La metal which belongs to the group-III metals transforms successively to the fcc phase at 1138 K and then to the double-hcp phase at 709 K: both transformations are martensitic in nature. Since La is the first member of the rare-earth metals and its properties are sometimes regarded as standard ones of the other rare-earth metals, studies on La from lattice dynamical viewpoint are very important to know characteristics of lattice instability of the rare-earth metals. First Stassis and

Zarestky⁽⁸³⁾ studied the $[110]TA_1$ phonon dispersion relation of the bcc-La metal by inelastic neutron scattering experiments. They found that such a branch is low-lying and frequency at the zone boundary is considerably low. Later Stassis and others⁽¹⁷⁷⁾⁽¹⁷⁸⁾ also performed inelastic neutron scattering studies on the fcc phase of La and observed that the $[111]TA$ branch, which corresponds to the $[110]TA_1$ branch of the bcc lattice, has low energy as a whole.

Recently Petry group⁽¹⁷⁹⁾ measured the phonon dispersion curves of the bcc La metal, which is single crystal grown *in situ* on the neutron-goniometer, at 1163 K and found that the dispersion relations resemble very much those of the bcc phases of Sc and the group IV metals. That is, the $[111]LA$ branch has a strong minimum at $2/3q_0$, where phonons are markedly damped and are well described by a damped oscillator function. The $[110]TA_1$ phonon branch is also low-lying as a whole. The eigenvectors of these low energy phonons are along the directions of the lattice distortions which are necessary to form the ω -structure and a close packed martensite structure, respectively. Such a situation means that the bcc group-III and group-IV metals have commonly low potential barrier to the lattice modulation towards MPT.

VII. Summary and Concluding Remark

In the present article, we review the results obtained by the recent neutron scattering studies on the premartensitic behaviours of the bcc-based metals and alloys. Since almost all MPT of these materials proceed through the periodic $(110)[1\bar{1}0]$ shear-and-shuffling process, one can suppose that some indications would appear on the $[110]TA_1$ phonon branch, which corresponds to atomic displacements along the $[110]$ direction, of their premartensitic states. Such a branch in the present subject is indeed low-lying. In addition, anomalies such as dip and softening have been found on the $[110]TA_1$ phonon branch of group IV metals, β -phase alloys, Ni-base alloys and others (see the literatures cited in the previous sections). However, except the case of NiTi, the softening is quite incomplete even just above M_s and, furthermore, phonon behaviours in the alkali metals are normal as a whole, although the Zener mode instability is strongly expected to appear. In any case, the soft mode theory cannot provide explanation of the MPT mechanism in the bcc-based materials.

As proved in our studies on the β_1 -phase alloys⁽¹¹³⁾⁽¹¹⁴⁾⁽¹¹⁷⁾, we can satisfactorily analyse the $[110]TA_1$ phonon branch accompanied by dips at $2/3q_0$ and/or q_0 by the interplanar force constant method. The dips are merely due to specific combinations of the second and third nearest neighbour force constants Φ_2 and Φ_3 . We must emphasize here that, if we know such force constants, or more favourably if we know their temperature dependence, we can predict the martensite structure to be formed in the β_1 -phases. Since the interplanar force constant analysis has been so far carried out only for Ti and the β -phase alloys, it seems significant to apply this

method to the other materials such as the alkali metals and the group-IV metals for understanding characteristics of the $[110]TA_1$ phonon branch in relation to the nature of MPT.

In the case of the Ni-base alloys, however, the interplanar force constant analysis is not adequate to examine the $[110]TA_1$ phonon dispersion curve. That is, the $[110]TA_1$ branches of NiTi and NiAl cannot be simulated by such a method. Therefore we must realize that this method is limited in its applicability. In addition, it is not clear why this method is effective to the β_1 phases and others and what is the origin of characteristics of the interplanar force constants. Concerning this problem, we must take anharmonicity into consideration as proposed by Krumhansl⁽⁵⁵⁾. For the present, it is important to examine temperature dependence of the third order elastic constants of the bcc-based materials, and to analyse anharmonic effects on the phonon behaviours. As suggested by several theoretical studies⁽¹³⁴⁾⁽¹⁴³⁾⁽¹⁶⁸⁾, phonon anomalies of the Ni-base alloys would be interpreted in terms of the electron-phonon interaction. In order to clarify the electronic effect, we must know the Fermi surface of materials in the present subject of study.

As regards the shape of the $[110]TA_1$ phonon dispersion curve, we must take a vacancy effect into consideration. In the bcc alkali metals, it has been expected that an interaction between the phonon branch and lattice defects takes place⁽⁴⁸⁾⁻⁽⁵⁰⁾. It is also believed that anomalously fast-self-diffusion in the bcc group-IV metals has a close relation to the phonon behaviours⁽⁸⁴⁾⁻⁽⁸⁷⁾. In addition, we have confirmed in the case of $AuCuZn_2$ ⁽¹¹³⁾⁽¹¹⁴⁾ that the quenched-in vacancies influence the shape of the $[110]TA_1$ branch. The vacancies enhance the lowering of the phonon branch and the $2/3q_0$ dip. Such a situation demands us to study in detail the effect of lattice defects on the phonon behaviours.

In the cases of the group-III and -IV metals, the $[111]LA$ branch in the bcc phase exhibits a drastic overdamping at $2/3q_0$ related to the ω phase formation. The ω phase is formed both in the bcc and martensite phases under stress field. Therefore, if the $2/3q_0$ anomaly on the $[111]LA$ branch in the bcc phase corresponds to a lattice instability towards the ω phase, we must find consistently a similar phonon anomaly related to the ω phase formation in the hcp martensite. So far, however, we have not found such an anomaly. There is also a problem for the bcc phase why only the anomaly concerned with the ω phase formation is drastic, while the premartensitic behaviour toward hcp is not outstanding. This problem seems to be the same as that in the β -phase alloys and others.

Concerning the anomalous elastic scatterings, we must clear up the followings. The one is the vacancy effect. Anomalous ω -like peaks appearing in the quenched $AuCuZn_2$ alloy, for example, are due to an ordered arrangement of vacancies produced inevitably in the B2 lattice⁽¹²²⁾. The B2-NiAl phase also exhibits the ω -like peaks and they are related to a certain kind of defect structure⁽¹¹⁹⁾. The other problem is concerned with martensitic

products or surface martensites. As claimed for the 7R structure in NiAl⁽¹⁷⁰⁾, we must probe whether the anomalous elastic scatterings are essential precursor of MPT or only due to vacancy or product effect, or both.

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