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LATTICE STABILITY AND SOFT MODES

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Abstract.— Relationships between displacive phase transitions and soft modes are discussed and illustrated using experimental examples. Ferroelectric and ferroelastic transitions are dealt with together with the "band-Jahn-Teller" and antiferromagnetic transitions which are closely connected with acoustic soft modes.

Since an acoustic mode softening has been observed in the vicinity of the martensitic transformation temperatures in B-phase alloys, it is of importance to discuss the close relation between the nucleation mechanism of martensite and the crystal anharmonicity near the $M_s$ temperature.

(I) Displacive Phase Transitions and Soft Modes in Non-metallic Materials.

(1) Condensation of $\Gamma_{15}$(optical) Mode at the Center of the Brillouin Zone ($BaTiO_3$)

The concept of "soft phonon" associated with a phase transition signifies a phenomenon in which a phonon mode, which coincides with a lower-symmetry structure, is very much amplified immediately before the onset of phase transition from a higher-symmetry structure. Fig. 1(a) shows a unit cell of perovskite structure (ABX$_3$) in which the A ions occupy the corners of a cube, X ions the face centres of this cubic and thus forming an octahedron and the B ions the body centre of the cube and the octahedron. Lattice vibrations in this unit cell can be described by the mutual vibrations among these three sublattices and by the displacement modes of the octahedron ($X_0$). The Brillouin zone is a simple cubic lattice as shown in Fig. 1(b). Soft modes which have been found so far are the $\Gamma_{15}$, $\Gamma_8$ and $\Gamma_{25}$ having their wave numbers at the $\Gamma$ point (zone center), at the $M$ point (1/2, 1/2, 0)a* and at the $R$ point (1/2, 1/2, 1/2)a* (zone boundaries), respectively.

$BaTiO_3$, having a perovskite structure, is a typical crystal which exhibits successive phase transitions with the soft modes playing an important role in the transitions. $BaTiO_3$ is paraelectric at high temperatures and the following displacive phase transitions occur successively upon cooling; (1) as the temperature approaches 393 K, the ions begin to be displaced, which results in a spontaneous polarization along the [001] direction, (2) upon further cooling to 278 K, the polarization vector changes its direction to [011] and (3) finally at the lowest transition temperature, 193 K, the polarization vector changes to the [111] direction. It is characteristic, however, that very slight distortions from the basic perovskite structure are associated with these transitions.

In terms of condensed soft modes these phase transitions can be understood as follows; the frequency, $\omega_{\Gamma_{15}}$, of $\Gamma_{15}$ mode ($q = 0$), which degenerates triply in the cubic lattice, decreases toward zero when the temperature approaches the transition point. Consequently, the restoring force is reduced resulting in the condensation of the ionic displacements corresponding to the $\Gamma_{15}$ mode, thus leading to the lower-symmetric static structure.

Since the tetragonal crystal can be formed by the $\Gamma_{15}$ mode having the [001] displacement, the temperature change in the frequency, $\omega_{\Gamma_{15}}(0)$, is given as

$$\omega_{\Gamma_{15}}^2(0) = A(T - T_0),$$

(1)
where $T_o$ represents the second order phase transition temperature. The first-order transition in BaTiO$_3$ takes place at 393 K which is higher than $T_o$.

When the tetragonal lattice is formed at 393 K, the triply degenerated $\Gamma_{15}$ mode is resolved into one mode which is parallel to the C axis, and into other modes of doubly degenerated components which are normal to the C axis direction in the tetragonal lattice. The latter components become soft again and one of them condenses at 278 K, inducing a transformation into an orthorhombic crystal, where the polarization changes its direction to $[011]$ because the $[010]$ direction of ionic displacement was coupled with that of already condensed $[001]$ mode. Finally, the retained $\Gamma_{15}$ mode with its $[100]$ displacement vector softens and condenses at 193 K, with the crystal structure consequently being changed into trigonal with $[111]$ polarization.

It has been proposed and is well known that the Lyddane-Sachs-Teller relation (1) exists between the frequencies of optical modes with $q = 0$, $\omega_{LO}^0(0)$ and $\omega_{TO}^0(0)$, and the dielectric constant, $\varepsilon(0)$:

$$\varepsilon(0) = \frac{\tau_{uu} L_0(0)^2}{\tau_{uu} T_0(0)^2}$$

(2)

Here, $\varepsilon(\omega)$ represents the optical part of the dielectric constant which is not dependent on temperature. If a soft mode exists and that the temperature variation of its frequency follows eq. (1) the dielectric constant $\varepsilon(0)$ should then obey the Curie-Weiss's law. Anomalies in the changes in specific heat and entropy observed at the transition temperature can be explained by the soft modes.

(2) Acoustic Soft Mode due to Piezoelectric Coupling ($KHPO_4$)

KDP and its isoforms represent an important class of hydrogen-bonded ferroelectrics (3). Brody-Cummins (2) have observed an acoustic soft mode in KHPo$_4$ (KDP) by means of Brillouin scattering technique. The KDP crystal belongs to the space group $I42d(D_2d^*)$ in the paraelectric phase and transforms to a ferroelectric phase $Pdd2(c13^9)$ when the transition temperature is attained. As shown in Figs. 2(a) and (b), four K-PO$_4$ groups are contained in the unit cell, and each PO$_4$ group is connected to four neighbouring PO$_4$ groups by $O-H-\cdots O$ bonds lying in the basal plane. Although the protons are thought to play an important role in the transition mechanism, the spontaneous polarization in the ferroelectric phase is parallel to the C-axis and essentially perpendicular to the proton motion. Thus the ferroelectric properties cannot be accounted for by the proton motion alone (see Fig. 2(b)). Therefore, the transition mechanism in these materials is that when the protons order, their motion being strongly coupled with an optic mode of the lattice, the proton-lattice interaction may cause a subsequent distortion of the K-PO$_4$ sublattices producing the spontaneous polarization. Among theoretical treatments of the phase transition, Kobayashi (4) has considered the coupling between the proton motion and an optic mode of the lattice. The treatment resulted in a transition involving a long-wavelength ($q = 0$) mode of the coupled system, and ordering of the...
of the protons on the $O--H--O$ bonds.

In the paraelectric phase, the free energy of the piezoelectric crystal is, in general, described as [5]

$$ F = \frac{1}{2}(\chi^{-1})^{-1} - \alpha \varepsilon + \frac{1}{2}C\varepsilon^2 $$

(3)

where $(\chi^{-1})^{-1}$ is the clamped inverse susceptibility, $\alpha$ the piezoelectric coefficient and $C$ the elastic stiffness at constant polarization. As is well-known, the free inverse susceptibility $(\chi^{-1})^{-1}$ and the elastic stiffness at constant electric field $C^E$ are, respectively, given by

$$(\chi^{-1})^{-1} = \frac{\alpha^2}{C} ; \quad C^E = C - \frac{\alpha^2}{(\chi^{-1})^{-1}}$$

(4),(5)

In KDP, since the transition is well described by the free energy

$$ F = \frac{1}{2}\alpha(T-T_0)^2 + \alpha \varepsilon + \frac{1}{2}C\varepsilon^2 $$

(6)

the following relations are experimentally confirmed: $(\chi^{-1})^{-1} = \alpha(T-T_0)$, $C = \text{constant}$

That the primary order parameter is indeed the polarization is clearly shown from the Landau theory. From eqs. (4) and (5),

$$(\chi^{-1})^{-1} = \alpha(T-T_0)$$

(7),(8)

The elastic constant $C^E$ at constant electric field as shown in Fig. 4 exhibits a hyperbolic decrease towards $T_0$ and reaches zero at $T_c$; the difference between the calculated second order phase transition temperature $T_0$ and the observed first order phase transition temperature $T_c$ was 4.3 K in KDP. This situation has been confirmed by Brody-Cummins in KDP.
The phase transition in KDP can be explained in terms of soft modes as follows; upon cooling the crystal from higher temperature towards \(T_c\), the optical mode begins to soften and softening of the acoustic phonon branch is consequently induced through the piezoelectric coupling.

(3) Ferroelastic Phase Transitions \((\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6\cdot\text{H}_2\text{O}, \text{Gd}_2\text{(MoO}_4\text{)}_3, \text{DyVO}_4 \text{ and Others})\)

The free energy as described by

\[
F = \frac{1}{2}(x_{\mu\nu})^2 + a \phi + \frac{1}{28}(T-T_0)x^2
\]

is considered next.

The following conditions are then valid:

\[
(x_{\mu\nu})^{-1} = \text{constant}
\]

\[
C^\phi = B(T-T_0).
\]

Following eqs. (4), (5) and (13),

\[
(x_{\mu\nu})^{-1} - \frac{T-T_0}{B(T-T_0)} = (x_{\mu\nu})^{-1} - \frac{a^2}{B(T-T_0)}
\]

\[
C^E = B(T-T_0).
\]

Fig. 5 The same as Fig. 3 should then result, and for the elastic instability transition

\[
T_c - T_0 = \frac{a^2}{B(x_{\mu\nu})^{-1}}
\]

can be obtained. These are schematically shown in Fig. 5, and a comparison with Fig. 3 clearly shows the interchangeability in the behaviour of the two parameters \(C^E\) and \((x_{\mu\nu})^{-1}\). Therefore, in this case \(C^E\) decreases linearly towards zero; in other words, a softening of acoustic mode occurs upon cooling from a high temperature to \(T_c\). This suggests that the primary order parameter is the homogeneous strain. The case has been named by Sewada et al. (7) as "proper ferroelastic" transition. Indeed this has been recently reported to be the case in the crystal \(\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6\cdot\text{H}_2\text{O}\) (lithium ammonium tartrate (LAT)) where no soft modes were observed in Raman scattering experiments (8). The transition has been described by the free energy as in eq. (11) and the ferroelectricity was indeed induced by the piezoelectric coupling with the polarization. Aizu (9) has defined "ferroelasticity" as follows; a crystal is said to be ferroelastic, when it has two or more orientation states in the absence of mechanical stress and can be shifted from one to another of these states by a mechanical stress; here any two of the states are identical or enantiomorphous in crystal structure and different in mechanical strain tensor at null mechanical stress. In ferroelastic crystals state shifts are expected to involve the appearance and vanishing of different domains and a square-hysteresis in the relationship between strain and stress.

So far, many crystals have been reported to undergo a phase transition at which the elastic constant vanishes. For example, in some crystals such as \(\text{TeO}_2\) (10) and \(\text{PrAlO}_3\) (11), it has been reported that the homogeneous strain is the sole order parameter for the transition. On the other hand, in the crystals such as \(\text{Gd}_2\text{(MoO}_4\text{)}_3\) (GMO) and \(\text{Tb}_2\text{(MoO}_4\text{)}_3\) (TMO) the coexistence of ferroelasticity and ferroelectricity has been observed in the low temperature phase although the transition can not be described by eq. (11), because of the appearance of the softening of zone-boundary phonons (12). GMO changes its phase at 433 K from the high temperature \(D_2d-P421m\) to the room temperature \(D_{2d}-P\bar{4}2m\) ferroelectric phase. The transition has been confirmed to arise from the \(q = (1/2, 1/2, 0)\) instability in the two-dimensional representation with \(D_{2d}\). Since the high temperature phase is piezoelectric, the polarization \(P_3\) and the strain \(x_6\) are coupled in such a way as to lead to the simultaneous change of the signs by an applied external stress or electric field (see Fig. 6).

In some crystals such as \(\text{DyVO}_4\) (13) and \(\text{TbVO}_4\) (14), the transition is known to take place primarily as a result of the cooperative Jahn-Teller instability based on the 4f electronic state. Because of the coupling between such mechanism and
strain, the softening of the acoustic phonon is induced (that is, "improper ferroelastic"). Moreover, it is of interest to see that the antiferroelectric property in a DyV\(_2\)O\(_4\) crystal is induced by the coupling between an optical mode \((q = 0)\) and the soft acoustic mode or, in other words, the low temperature phase of DyV\(_2\)O\(_4\) can be named an "improper antiferroelectric material" because it is induced by its ferroelasticity.

As described above, in the phase transitions which accompanies soft modes the crystal structures and characteristics of the low temperature phases depend upon what modes play the primary role and what kinds of couplings exist in the high temperature para-phase. The following Table 1 shows some examples of soft mode phase transitions in these non-metallic and metallic materials.

(II) Elastic Softening and Martensitic Transformation in Metals and Alloys.

"Enhanced Kohn anomaly" - Kohn (16) has pointed out that when the ion-ion and ion-electron interaction is only of the Coulombic type, an anomaly in the phonon dispersion relation \(q = 2K\) could appear due to the sudden change of the electronic screening effect for the lattice deformation corresponding to this condition, \(K\) is the Fermi momentum. This phenomenon has been called "Kohn anomaly" and it may be possible to understand the lattice instability based on the electron-lattice interaction in terms of this anomaly.

If the Kohn anomaly is somehow induced, a soft phonon with its wave vector \(q = 2K\) can be frozen-in. The following equations will represent such a condition:

\[
\omega_0^2 q_s = \omega_0^2 q_s \left[ 1 - \frac{|P_{q_s}|^2 x(q) v^2(q)}{1 + v_0 x(q)} \right] \tag{17}
\]

\[
P_{q_s} = \frac{q_0 x(q)}{\sqrt{v_0}} \tag{18}
\]

where \(\omega_0 q_s\) is the phonon frequency \((q\text{ wave vector in } s\text{ branch})\) without the electron-lattice interaction, \(V(q)\) is the Fourier component of the Coulomb interaction, \(v(q)\) is the interaction energy between ions and electrons, and \(X(q)\) is expressed as

\[
x(q) = \sum_{\delta q} \frac{\delta q}{\sqrt{v_0}} x(\delta q) \tag{19}
\]

where \(f(K)\) is the Fermi distribution function and \(\epsilon(K)\) the electronic energy. The second term of eq. (17) depends on the temperature change through the Fermi distribution function. If this term is large enough for specific values of \(q\) and \(s\), and the following relation is satisfied at the critical temperature \(T_c\),

\[
\frac{2}{\omega_0^2 q_s} = \frac{|P_{q_s}|^2 x(q, T_c)}{1 + v_0 x(q, T_c)} \cdot v_0^2(q) \tag{20}
\]

the lattice will become unstable with respect to this wave vector, thus leading to a phase transition due to the freezing-in of the vibrational mode. Since \(x(q)\) largely depends upon the shape of the Fermi surface, the anomaly in \(x(2K)\) will be enhanced if the shape of their surface changes successively from cubic to cylindrical and finally to a plane surface. This enhancement thus can be expected even in metals and alloys if the shape of their Fermi surfaces have at least a wide flat surface (see Fig. 7).

(1) Martensitic Transformations Associated with a remarkable Acoustic Mode Softening

(a) Band-Jahn-Teller Effect: Acoustic Soft Mode and Piezo-optic Coupling (\(V_3Si\) and \(Nb_2Sn\))

The cooperative Jahn-Teller transition, as described previously, showed that softening of the \(C_{ij}\)'s can be explained by the energy balance between
Table 1 Examples of phase transitions which accompany the soft modes. (15)

<table>
<thead>
<tr>
<th></th>
<th>Tc(K)</th>
<th>Crystal classes</th>
<th>Order parameter</th>
<th>Soft mode</th>
<th>Low tem. phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃</td>
<td>401</td>
<td>O₈-C₄ᵥ</td>
<td>Electrical polarization (P₁, P₂, P₃)</td>
<td>Optic mode 15 (q=0)</td>
<td>Ferroelectric</td>
</tr>
<tr>
<td>KDP</td>
<td>122</td>
<td>D₂h-C₂ᵥ</td>
<td>P₃</td>
<td>Optic mode (C₆₆)</td>
<td>Ferroelectric (Hydrogen-bonded)</td>
</tr>
<tr>
<td>LAT</td>
<td>98</td>
<td>D₂-C₂</td>
<td>Spontaneous strain(eₛ)</td>
<td>C₅₅</td>
<td>Ferroelastic (Ferroelectric)</td>
</tr>
<tr>
<td>TeO₂</td>
<td>P₆₃ at 8.86 Kbar at 293 K.</td>
<td>D₄-D₂</td>
<td>2e₃-e₁-e₂</td>
<td>C₁₁-C₁₂</td>
<td>Ferroelastic (Pressure induced)</td>
</tr>
<tr>
<td>PrAlO₃</td>
<td>151, 119</td>
<td>C₂ᵥ-C₅</td>
<td>e₁-e₂ Strain</td>
<td>C₁₁-C₁₂</td>
<td>? Ferroelastic</td>
</tr>
<tr>
<td>GDO</td>
<td>433</td>
<td>D₂d-C₂ᵥ</td>
<td>e₆</td>
<td>?/a(1,1,0) (Piezoelect. Coupling C₆₆)</td>
<td>Ferroelectric (Ferroelastic)</td>
</tr>
<tr>
<td>DyVO₄</td>
<td>13</td>
<td>D₄h-D₂h</td>
<td>e₁-e₂</td>
<td>C₁₁-C₁₂ (Cooperative Jahn-Teller Coupling)</td>
<td>Antiferroelectric</td>
</tr>
<tr>
<td>Nb₃Sn</td>
<td>45</td>
<td>O₈-D₄h</td>
<td>e₁-e₂</td>
<td>C₁₁-C₁₂ (Band Jahn-Teller coupl.)</td>
<td>Superconductive</td>
</tr>
<tr>
<td>In-Tl</td>
<td>195 (25T₁)</td>
<td>O₈-D₄h</td>
<td>e₁-e₂</td>
<td>C₁₁-C₁₂</td>
<td>? Antiferromagnetic</td>
</tr>
<tr>
<td>Mn-Cu</td>
<td>400 (11.74wt% Cu)</td>
<td>O₈-D₄h</td>
<td>e₁-e₂</td>
<td>C₁₁-C₁₂</td>
<td>?</td>
</tr>
</tbody>
</table>

Fig. 6 The reversible birefringence (Δnᵥ) vs. X and \( \Delta nₒ \) vs. E hysteresis loops for Gd₂(NoO₄)₂ [51].
the electron-lattice systems in the high temperature cubic phase. Also in R-tungsten structures (V3Si and Nb3Sn) having one-dimensional chain structure composed of V and Nb atoms, the 3d-band degeneracy has been lifted by the compensative distortion from cubic to tetragonal lattice and this Jahn-Teller mechanism for band-electron was accompanied by the softening of the shear constant C' = \(1/2(C_{11}-C_{12})\) above \(T_m\) (18).

Thus, the band Jahn-Teller transition can be expected to be an origin of elastic softening observed in the pre-transformation temperature region of metals and alloys, if though they must have the characteristic structures required for the satisfaction of the Jahn-Teller transition are met with.

The elastic softening as indicated in Fig. 8, by the temperature dependence of C'/C44, is observed in single crystals of V3Si (19). Simultaneously a rapid increase in attenuation for the [110][\(\{1\over 2\}\)] shear waves occurs below \(-100\) K, while \(T_m(M_b)\) is \(-21\) K. There are two types of crystals for either V3Si or Nb3Sn: one transforming and the other nontransforming. In the former a cubic-tetragonal structure phase transition occurs at a temperature \(T_m > T_c\), and in the latter no such transition occurs. The essential feature of C' for nontransforming V3Si and Nb3Sn (20) is that C' decreases with decreasing temperature, and at temperatures \(T \leq T_m\), C' becomes almost constant. Ting and Birman (21) have shown that this qualitative behavior can be explained by a new model of the electronic structure of R-tungsten compounds which has been presented recently by Gor'kov (22). On the other hand, Shirane and Axe (23) have measured phonon dispersion relations in Nb3Sn by inelastic neutron scattering. As an example of the remarkable temperature dependence of the soft TA1 phonon, the slope of dispersion lines at \(q = 0\) becomes zero with decreasing temperature and a kink arising from a Kohn anomaly appears at \(q = 2K_F\) (see Fig. 9). It is understood that since this acoustic phonon couples with the \(T_12(+)\) mode of optic phonon through the linear piezo-optic coupling, a displacement occurs corresponding to the optic-mode by the condensation of the acoustic-phonon even in the absence of the optic-phonon condensation (see Fig. 10).

The temperature dependence of the sublattice distortion has been examined by studying the temperature variation of the (300) reflection. The solid line shown in Fig. 11 to which the data are normalized, is the square of the tetragonal strain \((c/c_\perp)^2\), taken from recent X-ray measurements (24). This result shows that the internal sublattice displacements are proportional to the spontaneous tetragonal strain. The tetragonal strain components also transform as \(T_12(+)\), there exists also a linear coupling between \(u\) and \(T_12(+)\) optic-phonon displacements \(Q_1\). Thus

\[
F = (1/2m_1)^{\frac{1}{2}}(2u_{\perp 1}^2 + gQ_{\perp 1} \alpha + 1/20u_{\perp 1}^2) + \text{high-order terms.}
\]  

Neither \(u\) nor \(Q_1\) in this case can be identified as the order parameter. The appropriate order parameter is rather a linear combination of tetragonal strain and sublattice distortion obtained by minimizing the quadratic terms in eq. (21) with respect to \(Q_{\perp 1}\) (25).

Fig. 12 shows the energy spectra of [\(\zeta, 0\)] TA1 phonon mode with \(\zeta = 0.02\) in Nb3Sn (26). As \(T_m \leq 45\) K is approached, the intensity of central peaks rapidly increases, while the energy of soft TA1 modes moves to a finite but non-zero value. This fact cannot be accounted for on the basis of simple consideration in which the energy of the special phonon tends to zero at the transition temperature, but the central modes can be responsible for the critical scattering in the vicinity of \(T_m\). Shirane and Axe (23) have explained that, although the frequency \(\omega\) of acoustic phonons of \(q = 0\) may interact with other thermal phonons with the life time through Fig. 7: \(\mu(q)/\mu(0)\) vs. \(q\) relation: (1), (2) and (3) are the cases of one, two and three dimensions, respectively (17).
Fig. 8 Temperature dependence of \( \frac{(C_{11}-C_{12})/2C_{44}}{C_{44}} \) for a single crystal \( V_3Si \) (19).

Fig. 9 \([\zeta = 0]T_1\) phonon dispersion at small wave vector for three temperatures. The kink which appears at low temperatures was understood as a Kohn anomaly (23).

Fig. 10 Model of atomic shift in \( Nb_3Sn \)

Fig. 11 Temperature dependence of \((300)\) reflection. Solid line corresponds to the spontaneous tetragonal strain (24).

Fig. 12 Observed spectral profiles of \([\zeta = 0]T_1\) phonon mode in \( Nb_3Sn \) with \( \zeta = 0.02a^2 \) at several temperatures above \( T_M \) (23).
anharmonic terms, their population is subsequently disturbed. In the case of $w \ll r^{-1}$, the thermal phonons can locally reach a thermal equilibrium even in the distorted situation caused by the acoustic phonons in the crystal. Thus, an energy-dissipating process of the thermal phonons will correspond to the relaxation process, which can give rise to the central mode.

The central point of a Landau theory is the expansion of the free energy in powers of the order parameter and its gradients. The order parameter in Bhatt and McMillan's theory (27) is the d-band electron charge density. In the A-15 structure (or 6-tungsten compounds) there are three possible charge density waves (with wave vectors $(2\pi/a, 0, 0)$, $(0, 2\pi/a, 0)$ and $(0, 0, 2\pi/c)$) which open up an energy gap at the three X points. These three charge-density waves (CDW's) are coupled, respectively, to the optical phonons which pair the transition-metal atoms in the linear chains running in the x, y, and z directions. The optical phonons are coupled bilinearly to dilatations of the unit cell giving nine coupled modes. Each CDW is distorted situation caused by the acoustic phonons in the crystal. Thus, an

\[ yX (A = 1, 2, 3) \] are plotted in Fig. 16 for two temperatures as a function of the three principal symmetry directions.

McMillan's $w$ parameters turned to be weakly first order. The elastic behaviour (except for the shear constant $C_{44}$ whose temperature dependence can be accounted for in terms of inter-chain electronic terms) is well reproduced with a nonlogarithmic fit, as are the transverse sonic attenuation have been found not to be attributed to electron dynamics. At least the former is in agreement with impurity scattering.

Several experiments concerning pressure dependence of single-crystal elastic constants in $V_3Si$ and $V_3Ge$, etc. have been performed by Garcia et al. (28) and Larsen and Ruoff (29), while theoretical studies have been done by Ting and Ganguly (30) and others. Among these it is of importance to note that the first derivative of pressure of the shear modulus $C' = \frac{1}{2}(C_{11} - C_{12})$ is strongly temperature dependent and becomes negative at low temperatures. For example, a $dC'/dp$ vs. temperature relation for nontransforming $V_3Si$ is shown in Fig. 13. While the value of $dB^6/df$, where $B^6$ is the bulk modulus, is $-4$ at room temperature, it increases up to 7 at 13 K, suggesting that the decrease in volume makes the lattice stiff. The value of $dC'/dp$ is nearly constant ($\approx 1$) at the temperature range studied, while that of $dC'/dp$ is near unity at 300 K and decreases down to $-5$ at 13 K, suggesting that the pressure effect can enhance the softening of the $C'$ shear mode below~90K (29).

The pressure dependence of the three single-crystal elastic constants of $Nb_3Sn$ has been measured by means of the ultrasonic pulse superposition method from 13 to 300 K. The first pressure derivative of the soft shear modulus $1/2(C_{11} - C_{12})$ decreases almost monotonically with decreasing temperature, from +1.4 at 300K to $-1$ above the structural transformation temperature at 45 K (see Fig. 14). The pressure coefficient of the critical temperature corresponding to vanishing shear modulus agrees approximately with the pressure coefficient of the structural transformation temperature, which is of opposite sign to that in $V_3Si$ (31). The third-order elastic constants in Voigt notation for $Nb_3Sn$ are shown in Fig. 15. For comparison the corresponding data for $V_3Si$ (b) are also included. The sign and temperature variation are opposite to those for $V_3Si$ and their magnitude is about five times smaller than $V_3Si$. The opposite sign reflects the different sign of the tetragonal transformation strain $e_3 \approx (c/a - 1)$ in the two compounds. Above 100 K the Grüneisen parameter calculated from the elastic data in the anisotropic continuum approximation agrees well with the thermal Grüneisen parameter, but below 80K discrepancies between these two parameters attributed to precursor effects in the thermal strain up to 10 K above the structural transformation occur also in $Nb_3Sn$ as observed with X-rays (32). For $V_3Si$ there appears to be a correlation between these precursor phenomena and d-spacing fluctuations which show up in X-ray line broadening, but not in neutron scattering linewidths, and which have therefore been attributed to effects within a surface layer of the crystal (35).

The three elastic Grüneisen parameters $\gamma_\lambda (\lambda = 1, 2, 3)$ are plotted in Fig. 16 for two temperatures as a function of the three principal symmetry directions.
It is apparent that the absolute magnitude of the angular variation is only moderate at 300 K for the $\gamma_1$. However, at 50 K because of the shear mode softening the $\gamma_1$ for the two transverse modes are strongly direction dependent and show minima of $-33$ and $-5$ in [110] and near [111], respectively. In the vicinity of [111] both shear mode $\gamma$'s are negative. The large negative-mode gammas should give rise to negative thermal expansion below about 50 K in the cubic phase. Here, the microscopic first Gruneisen parameter is defined in terms of the first volume derivates of the lattice vibrational frequencies according to the following:

$$\gamma_1 = -\frac{V}{\omega_1} \left[ \frac{\partial \omega_1}{\partial V} \right]_T$$

(22)

The thermal or macroscopic Gruneisen parameter is defined by

$$\gamma = \frac{\beta V}{C_p}$$

(23)

$\beta$ is the volume thermal-expansion coefficient; $C_p$ the specific heat. This is in the quasiharmonic approximation given by the mode average (34).

$$\gamma = \frac{\sum_i \gamma_i}{\sum_i 1}$$

(24)

where $C_i$ denotes the Einstein specific heat of the $i$th mode.

---

Fig. 13 Temperature variation of the pressure derivatives of the elastic moduli for nontransforming $V_3Si$ (29).

Fig. 14 Squared natural velocity ratio $(w/w_o)^2$ vs. pressure for transverse mode in [110] with polarization in [110] for eight selected temperatures (31a)).

Fig. 15 Calculated third-order elastic constants in Voigt notation vs. temperature for $Nb_3Sn$ and $V_3Si$ (31b)).
Acoustic Soft Mode due to Antiferromagnetic Coupling (Mn-Cu and Mn-Ni)

Manganese-rich Mn-Cu alloys are usually called "high-damping alloys" and exhibit fairly high internal friction at room temperature after quenching from the high temperature phase (fcc). This large internal friction arises from the fcc-fct type martensitic transformation, where the (101) transformation twins are forced and an easy movement of the twin boundaries is thought to be responsible for the high damping property (35). As shown in Fig. 17, the internal friction peak and anomalous Young's modulus as observed at the As temperature in polycrystalline Mn-11.74wt%Cu alloys are shown in Fig. 17. Sugimoto et al. (36) have recently reported a similar elastic softening of C' upon cooling down to the transition temperature. It should be noted that the $T_N$ temperature is coincident with the Néel temperature ($T_N$) and accordingly the martensitic transformation can be induced by antiferromagnetic ordering. Therefore, the amount of transformation strains and the origin of softening of Young's modulus can be accounted for using long-range magnetic order parameters.

Makhrane and Gaunt (37) have tried a calculation of the variation of Young's modulus close to $T_N$ using a molecular field model by Weiss (38). However, they could not explain the elastic softening above $T_N$ since they neglected the role of short-range order in the temperature range above $T_N$.

Recently, Tsunoda and Wakabayashi (39) have studied the phonon dispersion relation in Mn-rich γ-Mn-Cu alloys by means of neutron inelastic scattering and have obtained results which are different in some important points from those of the measurements on Mn$_{85}$Ni$_{15}$Cu$_6$ by Lowde et al. (40). In the γ-MnCu alloy, the phonon which shows the softening at $T_M$ ($T_N$) is not the shear mode [110] but the [100]L branch and the cubic structure collapses because of the vanishing of $C_{11} + 2C_{12}$ not of $C_{11} - C_{12}$. The driving force to form the tetragonal structure may be a magnetic coupling force through magnetoelastic interactions.

Since $C_{11} + 2C_{12}$ has full cubic symmetry, the vanishing of this value does not necessarily lead to the tetragonal structure at $T_N$. Here, it should be remembered that the magnetic structure of γ-MnCu alloy has a tetragonal symmetry. The tetragonal axis coincides with the magnetic unique axis and the martensitic transformation temperature always coincides with the Néel temperature for γ-MnCu alloys. Furthermore, the tetragonality (1-c/a) is proportional to the square of the magnetic long-range order parameter (41). The assumption that the tetragonal structure is stabilized by magnetic coupling force after the cubic structure collapses by the vanishing of $C_{11} + 2C_{12}$ can successfully explain these characteristic properties of γ-MnCu alloy.

Saunders et al. (40) have reported softening of the q || [110], e || [110] acoustic mode in Mn-Ni (Mn-Ni-C) systems that exhibits a similar fcc-fct transition; the γ-Mn-Ni-C alloys have qualitatively the same diagram as Mn-Ni alloys (41).

The unit cell dimension measurements for two crystals, with 9.2 ± 0.2 and 8.8 ± 0.2 atomic percent nickel, respectively are reported in Fig. 18. Both undergo a structure transition, the latter exhibiting a very nearly second order transition to a tetragonal condition with $c > a$. Fig. 19 shows the temperature dependence of the elastic constants for the 9.2 ± 0.2 at % Ni specimen. While variation of $C_{14}$ is qualitatively normal, $C_{11}$ is in a much more advanced state of collapse. With...
reducing temperature, $C_{11}$ falls into a severe decline, sufficient to induce extremely low values of $1/2(C_{11} - C_{12})$ and hence to result in the onset of a martensitic transformation at about $123 \pm 2$ K. The temperature dependence of $C_{11}$ should be interpreted as follows: the transition is first order, $C_{11}$ experiences a small downward discontinuity of 0.017 Pa at about 125 K and rises again thereafter towards normal values, as though a critical state has been closely bypassed. The anomalous slopes in Fig. 19 signify that considerable mode softening is endured in many of the branches of lattice vibration; however, no elastic constant attains zero at the transition, and even the principal soft mode, $[110]T_1$, still has a value of $1/2(C_{11} - C_{12}) = 5(\text{GPa})$ at $M_s$.

The low-\(q\) region of the transverse [\(q \leq 0\)] mode, which is highly anomalous, is exhibited in detail for two temperatures in Fig. 20. The phonon energies at 175 K ($\sim M_s$), are known to within a standard deviation of 54 \(\mu\)eV as a result of high-quality analytical procedures; the corresponding value at room temperature is 38 \(\mu\)eV. A severely non-linear $w(q)$ is revealed, which has been named "spoon" because of its shape. Room temperature is evidently close enough to the transition temperature for the phonon energies to be significantly softened near to the origin $\Gamma$ of the Brillouin zone. On the other hand, 77 K appears to be sufficiently far below $M_s$ for the phonon dispersion to be restored nearly, but not quite, to the normal behaviour.

The general idea that the abnormal reduction of $C_{11}$ observed here goes together with the collapse of ferromagnetism in these alloys and its progressive replacement by itinerant-electron antiferromagnetism is consistent with the appearance of severe magneto-elastic anomalies in comparable manganese alloys (43). The unifying feature would seem to be the highly unstable magnetic moment developed in fcc alloys in this region of the periodic table and the consequent large electron-phonon interaction.

(c) Acoustic Soft Mode due to Electronic Coupling (In-T1, In-Cd and In-Pb)

In-T1 alloys in the composition range 16 to 31 at \% Tl undergo a fcc-fct martensitic transformation resembling that in In-Tl alloys (42), with softening of the transverse acoustic $[110]T_1$ phonon polarised along $[110]$. The associated elastic constants are marked by an uniquely low value of $C_{11}$, lower in this case than $C_{44}$.

In Fig. 17 is shown the internal friction peak and elastic anomaly near the transition temperature in Mn-11.74\%Cu alloy (36).

![Fig. 17 Internal friction peak and elastic anomaly near the transition temperature in Mn-11.74\%Cu alloy (36).](image-url)
the C' softening clearly occurs in the vicinity of the transformation temperatures. However, at the transition temperature C' does not drop to zero, but has a finite value which is larger for the In-Pb alloy than for the In-Cd alloy.

A recent electron diffraction study (47) has revealed remarkable two-dimensional diffuse scattering on the \(110\) planes of the reciprocal lattice. This might be due to the existence of transverse acoustic phonons with low-frequencies with displacement vectors along the [110] direction in the crystal.

A mechanism of phonon-coupling which might occur in the In-alloys has been explained by Nittono et al. (48) as follows: The coupling and freezing-in of two phonons, such as \((q // [110], e // [110]) + (q // [101], e // [101])\), can give a necessary shear which is expressed as \(2\eta\) where \(2\eta\) is the shear angle. Table 2 shows the types of the transformations, coupled phonons and double shear systems together with the temperature hysteresis \((\Delta T = A - M)\) and volume changes at the transition temperatures.

![Fig. 18 Lattice parameters, measured by neutron diffraction:](image)

(i) for a MnNiC alloy with 9.2±0.2at%Ni, 6.1±0.2at%C;
(ii) for a similar alloy with 8.6±0.2at%Ni, 5.6±0.3at%C (40).

In-based alloys transform in general from fcc to fct structure with a very small change in volume. The origin of phase transition in In-based alloys is thought to be due to the strong electron-phonon coupling, so that the electronic energy decrement depends upon the magnitude of the tetragonal strain (49). Hence, the thermodynamic potential \(\Phi(T,\eta)\) of the crystal can be expanded in powers of the order parameter \(\eta\) which defines the deviation from cubic symmetry. Figs. 23(a) and (b) show the thermodynamic potential curves vs. strain parameter calculated at their transition points in In-Tl, In-Cd and In-Pb alloys. The minima in the curves correspond to the fcc phase \((\eta = 0)\) and the fct phase \((\eta = \eta_M)\), respectively. The fcc-fct transformation thus represents a transition which occurs between two minima and the peak height between two minimum states may be considered similar to the activation energy required for the transition. The height of the peaks increased in the order In-Tl, In-Cd and In-Pb alloys (50), suggesting that the transition deviates more and more from a second order type for the same alloy sequence. Such a deviation from the second order transition may also result in differences in mobility of interface and twin boundaries among In-Tl, In-Cd and In-Pb alloys. The effect of anharmonic lattice vibrations appears to be dominant in the martensitic transformations of In-Cd or In-Pb alloys which deviate slightly from the second-order transition, when compared to the In-Tl alloy.
Fig. 20 Points show the measured "soft" phonon dispersion law for small q vectors along the [110] direction in the MnSeMg66 alloy of Figs. 18 (ii).

Table 2: Coupled phonon systems and other characteristics in phase transformations of Indium alloys (48).

<table>
<thead>
<tr>
<th>Type</th>
<th>Type of phase transition</th>
<th>Alloying composition</th>
<th>$\Delta T = A_g - M_g$</th>
<th>$\Delta V/V(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{fcc} \neq \text{fct}(c/a &gt; 1)$</td>
<td>$\text{In-(18~\sim 30\text{at%})Tl}$</td>
<td>0~2</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>$\text{In-(4~\sim 5.5\text{at%})Cd}$</td>
<td></td>
<td>2~3</td>
<td>0.030</td>
</tr>
<tr>
<td>II</td>
<td>$\text{fcc} \neq \text{fct}(c/a &lt; 1)$</td>
<td>$\text{In-(28~\sim 36\text{at%})Pb}$</td>
<td>10~15</td>
<td>~0.3</td>
</tr>
<tr>
<td>III</td>
<td>$\text{fct}(c/a &gt; 1) \neq \text{fco} \neq \text{fct}(c/a &gt; 1)$</td>
<td>$\text{In-(12~\sim 16\text{at%})Pb}$</td>
<td>10~15</td>
<td>~0.3</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{fct}(c/a &lt; 1) \neq \text{fct}(c/a &gt; 1)$</td>
<td>$\text{In-(13~\sim 15\text{at%})Sn}$</td>
<td>30~40</td>
<td>~0.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Type of phase transition</th>
<th>Coupled phonon system $\mathbf{q} \approx 0[110], \mathbf{e}//[11\overline{1}]$</th>
<th>Double shear system $(110)[1\overline{1}0]2\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\text{fcc} \neq \text{fct}(c/a &gt; 1)$</td>
<td>$\mathbf{q} \approx 0[101], \mathbf{e}//[10\overline{1}]$</td>
<td>$(101)[10\overline{1}]2\varepsilon$</td>
</tr>
<tr>
<td>II</td>
<td>$\text{fcc} \neq \text{fct}(c/a &lt; 1)$</td>
<td>$\mathbf{q} \approx 0[01\overline{1}], \mathbf{e}//[01\overline{1}]$</td>
<td>$(01\overline{1})[01\overline{1}]2\varepsilon$</td>
</tr>
<tr>
<td>III</td>
<td>$\text{fct}(c/a &lt; 1) \neq \text{fco}$</td>
<td>$\mathbf{q} \approx 0[01\overline{1}], \mathbf{e}//[01\overline{1}]$</td>
<td>$(01\overline{1})[01\overline{1}]2\varepsilon$</td>
</tr>
<tr>
<td>IV</td>
<td>$\text{fct}(c/a &lt; 1) \neq \text{fct}(c/a &gt; 1)$</td>
<td>$\mathbf{q} \approx 0[01\overline{1}], \mathbf{e}//[01\overline{1}]$</td>
<td>$(01\overline{1})[01\overline{1}]2\varepsilon$</td>
</tr>
</tbody>
</table>
Anharmonicity in the Vicinity of $M_s$ in $R$-Phase Alloys

Several anomalies can be observed as phenomena preceding the martensitic phase transformation in many $R$ phase alloys. Among them, elastic constant anomalies related to the acoustic modes are typical. That is, elastic stiffness constants $C'$ and $C_s$, which correspond respectively to the $TA_1$ and $TA_2$ modes at the Brillouin zone center, exhibit a softening behaviour above the $M_s$ point. $C' = (C_{11} - C_{12})/2$, is the resistive stress to the $(110)$ shear and its softening is accepted at present to be common in the $R$ phase alloys undergoing the martensitic transformation (51). The $C_s$ softening, recently found near the $M_s$ point, in many $R$ phase alloys by the present authors (52-54), is responsible for the $(112)\{111\}$ shear.

Examples of the elastic anomalies mentioned above are shown in Figs. 24 and 25. Referring to these results, several problems related to the transformation mechanism in the $R$ phase alloys will be considered. The $R_1$ phase has one of the following ordered structures such as the CsCl, Fe$_3$Al and Heusler types. The transformation from this $R$ phase to the $2H$ or $9R$ (or $18R$) type of the close-packed layer martensite will be discussed.

(a) Acoustic Softening and Burgers Model.

From the point of view of the crystal geometry, martensite is formed through two kinds of shear processes in the $R_1$ lattice: the $(110)\{111\}$ and $(110)\{110\}$ shears. The former is responsible for changing the $(110)_B$ planes into the close-packed planes of the martensite, while the latter is responsible for the stacking sequence of these close packed planes. Although proposed originally by Burgers (56) for the bcc to hcp transformation of Zr metal this scheme is usually referred to as the Burgers relation.

The temperature dependence of the elastic constants as shown in Figs. 24 and 25 are closely related to the Burgers model, the softening of the acoustic modes $C'$ and $C_s$ implies a decrease of resistive stresses against the shears in the Burgers relation. The Burgers model thus seems to be valid for the $R$ phase alloys because softening of $C'$ and $C_s$ really occur. The Burgers model assumes that the $(112)\{111\}$ shear occurs first followed by the $(110)\{110\}$ shear. However, there is no evidence for such a sequence, as discussed in a previous paper (54). The martensite formation in $R$ phase alloys is proposed to proceed through the reverse sequence, because the lattice softenings occur in the $C'$ mode first and then in the $C_s$ mode (Figs. 24 and 25). In other words the $R_1$ lattice becomes unstable with respect to the

Fig. 22 Temperature dependence of $1/2(C_{11}-C_{12})$ calculated in In-32at%Pb and In-4.4at%Cd alloys (46).

Fig. 23 Free energy curves as a function of the spontaneous strain in the vicinity of the transition temperature (a); In-4.4at%Cd and In-21 at%Tl, (b); In-32at%Pb and In-4.4at%Cd alloys (46).
(110)[110] shear first and then the (112) shear. That is, the shear sequence necessary to form the martensite must be reverse of that described in the original Burgers relation.

Symmetry consideration also seems to support this argument. For example, lattice deformation, due to freezing-in of the $C_9$ mode in the $D_{2h}^{15}$ lattice with the Heusler type structure, causes a symmetry change from $Fm3m$ ($C_{2h}^{14}$) to $I4mm$ ($D_{2h}^{15}$). The martensite that is produced in reality, however, belongs either to the space group $Pmm$ ($D_{2h}^{15}$) (2H type martensite) or to $P2/m$ ($C_{2h}^{14}$) (18R type martensite). Thus, if the (110)[110] shear occurs first, the martensite formation must proceed through a two-step symmetry change.

On the other hand, when the (110)[110] shear occurs first, the symmetry change occurs only once and the lattice produced by this shear belongs to the same space group as that of the final martensite. The subsequent (110)[110] shear does not produce any symmetry change. Many experimental results obtained so far prove that such a single step transition is realized. An essential role of the (110)[110] shear in the scheme is to lower the lattice energy of the 2H or 9R (or 18R) martensite. This is because the lattice energy of such a stacking structure modulated by the (110)[110] instability will be minimum when the basal planes are close-packed.

(b) Third Order Elastic Constants and Lattice Anharmonicity

One of the most important characteristics of the elastic modes is its non-linear temperature change as revealed in Figs. 24 and 25. The $C'$ mode, for example, gradually decreases with decreasing temperature but, near the $M_s$ point, it begins to deviate from a linear change. The temperature changes of $C_{44}$ and $C_6$ also exhibit non-linear phenomena. The non-linearity in every mode appears simultaneously and cooperatively at nearly the same temperature as indicated by the arrows. This means that the elastic modes are correlated and an anharmonic effect follows.

The temperature dependence of any elastic mode is due to the existence of a crystal anharmonicity. Therefore, $B_1$ phases are anharmonic even before exhibiting the non-linearity. The non-linear phenomena of the elastic modes may possibly result from a remarkable enhancement of the crystal anharmonicity. From this point of view, the third order elastic constants in several $B_1$ phase alloys are now being studied. Results obtained so far are presented below and the anharmonic effect on the martensitic transformation is discussed.

The ultrasonic velocity changes due to uniaxial pressure, measured in Au-33.0 at%Cu-47.0at%Zn alloy is shown in Fig. 26. By substituting the velocity change $(\delta V/\delta P)_0$ into the Thurston-Brugger equation (57), six kinds of the third order elas-

![Fig. 24 Temperature changes of elastic modes in the Au-35.0at%Ag-47.5 at%Cd alloy.](image1)

![Fig. 25 Temperature changes of elastic modes in the Cu-17.0at%Al-14.3 at%Zn alloy (55).](image2)
The stability condition of the R\textsubscript{1} \textsubscript{2} 4 6 8 10 12 phase against the above defined strain in the 3\textsubscript{i} constants \(C_{i}\) can be obtained. Table 3 shows these \(C_{i}\) for Au-33.0at\%Cu-47.5at\%Zn and Cu-17.0at\%Al-14.3at\%Zn alloys.

It is remarkable that all the third order elastic constants \(C_{i,j,k}\) are negative and their absolute values are very large. Such characteristics have also been observed in the \(B_{1}\) phases of Cu-Zn (58) and Cu-Zn-Al (59) alloys. The \(B_{1}\) phase is thus in a considerably anharmonic state as this anharmonic effect plays an important role in the transformation mechanism.

In discussing the lattice instability from a viewpoint of the free energy as a function of strain, third order terms must be included because this is the minimum order of approximation. The free energy change as a function of strain is thus calculated by using the obtained second and third order elastic constants. Results for Au-33.0at\%Cu-47.0at\%Zn are shown in Fig. 27. The strain is the same as used by Clapp (60): nearly a pure Bain strain with no volume change. \(K\) in Fig. 27 is defined by \(\frac{2}{3} \frac{\partial^{2} F}{\partial \tau^{2}}\), where \(F\) and \(\tau\) are respectively the free energy change and the strain, and implies a constant restoring force.

The stability condition of the \(B_{1}\) phase against the above defined strain is expressed as \(K > 0\). Therefore, the \(B_{1}\) phase becomes unstable near \(\tau = 0.04\), when the free energy barrier for transformation is only \(1.0 \times 10^{-3}\) eV or 11.6K per atom. This value may be an underestimated one, because (i) fourth order elastic constants are not considered and (ii) the strain used is oversimplified. However, it should be emphasized that the energy barrier to form the martensite is considerably lowered by the anharmonic effect.

Substituting the third order elastic constants into the Thurston-Brugger equation, the compressive stress derivatives of the second order elastic constants as a function of stress direction can be obtained. Results are shown plotted in Figs. 28 and 29 for \(C'\) in Cu-17.0at\%Al-14.3at\%Zn alloy and in Fig. 30 for \(C_{S}\) in Au-33at\%Cu-47at\%Zn alloy. The compression axis is changed in Fig. 28 from [001] to [110] on the (110) plane while in Fig. 29 from [001] to [110] on the (110) plane. The direction of the compressive stress in Fig. 30 is changed in the (110) plane. The \(C'\) and \(C_{S}\) modes in a similar behaviour to that shown in these figures.

It is clear that the stress derivatives are considerably anisotropic. They are negative or positive with respect to the stress directions. The negative derivative means that the corresponding second order elastic constant becomes soft while the positive implies hardening. In any case, the derivative has the minimum value for a compressive stress direction with high symmetry. This means that the lattice instability in the \(B_{1}\) phase will...
Table 3 Examples of the obtained third order elastic constants (TPa in unit)

<table>
<thead>
<tr>
<th>$C_{ijk}$</th>
<th>Au-33.0Cu-47.0Zn</th>
<th>Cu-17.0Al-14.3Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{111}$</td>
<td>-1.58</td>
<td>-1.55</td>
</tr>
<tr>
<td>$C_{112}$</td>
<td>-0.65</td>
<td>-0.70</td>
</tr>
<tr>
<td>$C_{123}$</td>
<td>-0.69</td>
<td>-0.84</td>
</tr>
<tr>
<td>$C_{144}$</td>
<td>-0.70</td>
<td>-0.76</td>
</tr>
<tr>
<td>$C_{166}$</td>
<td>-0.63</td>
<td>-0.76</td>
</tr>
<tr>
<td>$C_{456}$</td>
<td>-0.57</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

Fig. 28 Pressure derivatives of $C'$ as a function of stress direction in Cu-17.0at%Al-14.3at%Zn and pure Cu.

Fig. 29 Pressure derivatives of $C'$ as a function of stress direction in Cu-17.0at%Al-14.3at%Zn and pure Cu.

Fig. 30 Derivative of $C_8$ as a function of stress direction in Au-33.0at% Cu-37.0at%Zn alloy.
progress under the stress field along such a direction. Suggestions, based on the above results can be advanced; which may not only be relevant, but even important, to the nucleation problem in martensite transformation. Many nucleation models have been so far proposed (63). The models mostly regard certain kinds of lattice defects as the nucleation centers (64). On the other hand, any \(B_1\) phase contains a number of defects distributed randomly. However, not all but only a limited number of defects will be activated as nucleation centers, even if they have the same capability of becoming nuclei. Thus the question remains to be answered what defects and why only such defects are activated as nucleation centers.

Any defect, however, can be replaced by a certain kind of localized stress field, which will be remarkably anisotropic. Regions around the stress field can be activated as nucleation centers, if the local field has the largest component along the direction corresponding to the minimum pressure derivative, such as [001] in Fig. 28. To emphasize in other words, the martensitic nucleation mechanism is closely related to the anharmonic effect.

(c) Possibility of Electron-Lattice Interaction

The lattice softening is incomplete and does not attain a value zero even at the \(M_S\) temperature. An energy barrier exists which prevents the martensite formation and hence there must be a certain kind of mechanism to overcome this energy barrier. The phonon anomaly found in the \(B_1\) phase of \(AuCuZn_2\) alloy by Mori et al. (61) may provide an answer to this problem. The phonon dispersion curve of the \(TA_1\) branch with \(q \parallel [110]\) and \(e \parallel [110]\) exhibits near the \(M_S\) point a drop at \(q - 2/3[110]\). Correspondingly, the neutron diffraction pattern shows an anomalous reflection at \((H + 2/3, K + 2/3, 0)\) around the fundamental reflections with \(H + K = 4n\). The anomalies are regarded as the enhanced Kohn anomaly. If so, this means that the Fermi surface satisfies a nesting condition at \(q - 1/3[110]\). When the 18R martensite is formed, on the other hand, a new Brillouin zone boundary is formed at \(q - 1/3[110]\) i.e. the Brillouin zone boundary touches the nesting Fermi surface. Therefore, by such a transformation, the electronic free energy of the alloys is lowered.

Recently, anomalous diffuse scattering has been observed as shown in Fig. 31 during X-ray studies of the \(B_1-Cu-17.0\%Al-14.3\%Zn\) phase near the \(M_S\) point (55). The anomalies appear near the reciprocal lattice points such as 130 and 310 corresponding to the X point of the Brillouin zone. They are not due to Bragg reflection because the structure factors are zero at such points. The anomalies in diffuse scattering are regarded as Kohn anomaly as in the case of \(AuCuZn_2\) alloys (61). So we can suppose that the Fermi surface satisfies a nesting condition at \(q - 1/2[110]\). In the present case, the 2H martensite can be produced forming a new Brillouin zone boundary which contacts the Fermi surface at \(q - 1/2[110]\).
The above situation strongly suggests the existence of the Peierls type of lattice instability (62) and if true, the strain free energy preventing the martensite formation will be easily compensated by such an electron-lattice interaction. This argument, however, is based on an assumption that the observed anomaly in diffuse scattering is a Kohn anomaly. In order to ascertain whether this anomaly corresponds to the origin of the martensitic transformation, it is essential to elucidate whether an electron-lattice interaction is possible or not in these martensite R-phase alloys.

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