The Variation of Young's Modulus of a Binary Body-Centered Alloy caused by the Formation of Superlattice

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I. Introduction

Young's modulus of superlattice alloys such as Cu_3Pd, Cu_3Au, $CuAu$, $CuPd$, $CuZn$, Fe_3Al, etc. has been measured by Roehl[1], Siegel[2], Koester[3], Rinehart[4], Kubo[5], Masumoto and Saito[6] etc. These results show that Young's modulus of alloys such as Cu_3Pd, Cu_3Au and $CuZn$ increases with the formation of superlattice, while on the contrary that of such alloys as $CuAu$, $CuPd$ and Fe_3Al decreases. For the case of $CuAu$ a slight change in the crystal structure occurs by the formation of superlattice but not for the cases of Cu_3Au and $CuZn$. The temperature variation of Young's modulus of the latter two alloys, as shown in Fig. 1 (a), (b) is quite similar to the variation of the degree of order for these alloys with temperature, as shown in Fig. 1 (c), (d) which was calculated by the approximate method of Bragg-Williams[7] or Bethe[8]. It seems that there is hitherto no theoretical explanation for this fact. Therefore in order to explain this behavior for the case of beta brass (CuZn) we developed a qualitative theory, based upon the Bragg-Williams' approximation.

II. The relation between Young's modulus and the degree of order

Here it is assumed that the interatomic force is central i.e. a function of atomic distance r, and acts between the nearest neighbor atoms only. The body-centered cubic lattice of such a binary alloy as beta brass can be divided into two simple cubic lattices I and II. In Fig. 2 which shows an unit cell of a body-centered cubic lattice having the
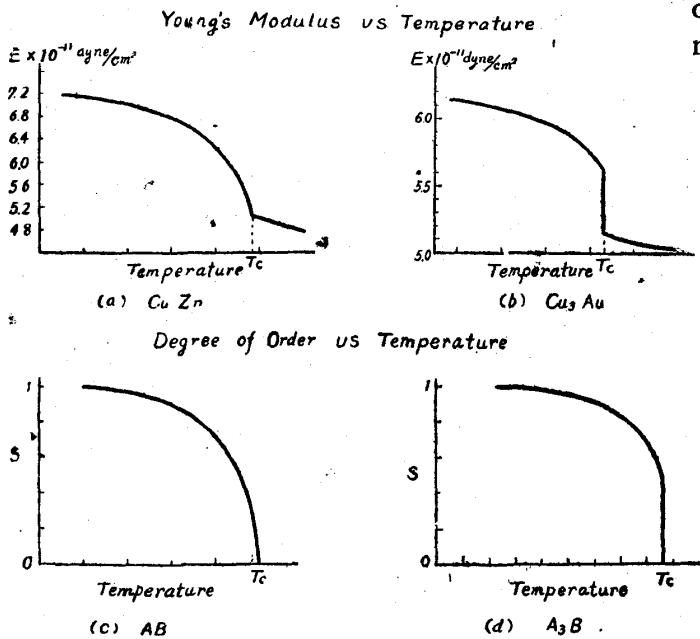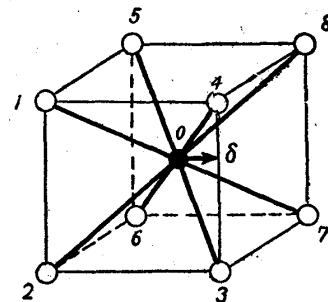

Young's Modulus vs Temperature

(a) CuZn

(b) Cu_3Au

Degree of Order vs Temperature

(c) AB

(d) A_3B

Fig. 1.

○ I site

● II site

Fig. 2.

edge length a, the cube corners represent I sites and the cube center II site. Using the notation of Fowler-Guggenheim[9] and Takagi[10] number of A atoms (for instance Cu atoms) on the I sites in the state of the degree of order S is $\left[\frac{A}{I}\right]$. We define similarly $\left[\frac{A}{II}\right]$, $\left[\frac{B}{I}\right]$ and $\left[\frac{B}{II}\right]$. According to Bragg-Williams' approximation, we get,

$$\left[\frac{A}{I}\right]=\frac{1+S}{2}N, \quad \left[\frac{A}{II}\right]=\frac{1-S}{2}N \\ \left[\frac{B}{I}\right]=\frac{1-S}{2}N, \quad \left[\frac{B}{II}\right]=\frac{1+S}{2}N \quad (1)$$

in which N is number of A or B atoms (the total number of atoms is $2N$). Denoting the interaction energy between A atoms by V_{AA}, that between B atoms by V_{BB} and that between A and B atom by $V_{AB}(=V_{BA})$, those are functions of interatomic distance r only by the said assumption. It may not be unreasonable to suppose that $\frac{1+S}{2}$ of A atoms and $\frac{1-S}{2}$ of B atoms coexist on each I site in the state of the degree of order S. These atoms contribute $V_{IIA}(r)$ defined by the $Eq.(2)$ to the potential energy of A atom on II site.

$$V_{IIA}(r)=\frac{1+S}{2}V_{AA}+\frac{1-S}{2}V_{BA}. \quad (2)$$

Similarly we define $V_{IIB}(r)$, $V_{IA}(r)$ and $V_{IB}(r)$.

(i) Young's modulus in the [100] direction

Assume that the unit cell shown in Fig. 2 suffers an elongation 2δ in the [100] direction without lateral contraction. Then the shortest interatomic distance $r_0\left(=\frac{\sqrt{3}}{2}a\right)$ becomes r as given below;

$$r=(r_0^2+\delta^2-2r_0\delta\cos\theta)^{1/2}$$

where θ is the angle between r_0 and δ.

Then $V_{IIA}(r)=V_{IIA}(\sqrt{r_0^2+\delta^2-2r_0\delta\cos\theta})$

$$=(V_{IIA})^0-\delta\cos\theta\left(\frac{dV_{IIA}}{dr}\right)^0$$
$$+\frac{\delta^2}{2}\left[\frac{\sin^2\theta}{r_0}\left(\frac{dV_{IIA}}{dr}\right)^0\right.$$
$$\left.+\cos^2\theta\left(\frac{d^2V_{IIA}}{dr^2}\right)^0\right], \quad (3)$$

where $(V_{IIA})^0$, $\left(\frac{dV_{IIA}}{dr}\right)^0$ and $\left(\frac{d^2V_{IIA}}{dr^2}\right)^0$

represent values of V_{IIA}, $\left(\frac{dV_{IIA}}{dr}\right)$ and $\left(\frac{d^2V_{IIA}}{dr^2}\right)$ at the point $r=r_0$ respectively. In the above expression higher order terms of small quantity δ was retained to the second order term.

Assuming further that

$$\left(\frac{dV_{IIA}}{dr}\right)^0=0, \quad \text{etc,} \quad (4)$$

$i.e.$ $\left(\frac{1+S}{2}\right)\left(\frac{dV_{AA}}{dr}\right)^0+\left(\frac{1-S}{2}\right)\left(\frac{dV_{BA}}{dr}\right)^0$
$$=0, \quad \text{etc,} \quad (4)'$$

then $Eq.(3)$ becomes

$$V_{IIA}(r)=(V_{IIA})^0+\frac{\delta^2}{2}\cos^2\theta\left(\frac{d^2V_{IIA}}{dr^2}\right)^0. \quad (5)$$

Let the potential energy between A atom at the cube center O and atoms in the (100) plane containing 1, 2, 6 and 5 atoms be $\phi_{IIA}(r)$, and

$$\phi_{IIA}(r)=\sum_{1,2,6,5}V_{IIA}(r)$$
$$=\sum_{1,2,6,5}\left[(V_{IIA})^0+\frac{\delta^2}{2}\cos^2\theta\left(\frac{d^2V_{IIA}}{dr}\right)^0\right]$$
$$=(\phi_{IIA})^0+\frac{4}{6}\delta^2\left(\frac{d^2V_{IIA}}{dr^2}\right)^0.$$

The force f_{IIA} which acts between A atom on II site and atoms on the (1, 2, 6, 5) plane, caused by the elongation 2δ of the unit cell in the [100] direction, is given by

$$f_{IIA}=-\frac{-\partial\phi_{IIA}(r)}{\partial\delta}=-\frac{4}{3}\delta\left(\frac{d^2V_{IIA}}{dr^2}\right)^0.$$

By the substitution with $Eq.(2)$

$$f_{IIA}=-\frac{4\delta}{3}\left\{\left(\frac{1+S}{2}\right)\left(\frac{d^2V_{AA}}{dr^2}\right)^0\right.$$
$$\left.+\left(\frac{1-S}{2}\right)\left(\frac{d^2V_{AA}}{dr^2}\right)^0\right\}.$$

Using the following parameters ξ_{AA} etc.,

$$\frac{1}{3}\left(\frac{d^2V_{AA}}{dr^2}\right)^0=\xi_{AA} \\ \frac{1}{3}\left(\frac{d^2V_{BB}}{dr^2}\right)^0=\xi_{BB} \\ \frac{1}{3}\left(\frac{d^2V_{BA}}{dr^2}\right)^0=\xi_{BA} \quad (9)$$

$$f_{IIA}=-4\delta\left\{\left(\frac{1+S}{2}\right)\xi_{AA}+\left(\frac{1-S}{2}\right)\xi_{BA}\right\}.$$

Similary in regard to B atom on II site,

$$f_{IIB}=-4\delta\left\{\left(\frac{1-S}{2}\right)\xi_{BB}+\left(\frac{1+S}{2}\right)\xi_{BA}\right\}.$$

Denoting the surface density of atoms on the (100) planes by $\sigma_{(100)}$, the unit area of

the (100) plane containing the atom O at the cube center, contains $\left(\dfrac{1-S}{2}\right)\sigma_{(100)}$ of A atoms and $\left(\dfrac{1+S}{2}\right)\sigma_{(100)}$ of B atoms, since this (100) plane belongs to the II lattice. Therefore the force which acts between atoms on this unit area and those on the unit area of the neighbor (100) plane containing 1, 2, 6 and 5 atoms, is

$$\mathbf{F} = \sum_{\text{unit area}} (f_{IIA} + f_{IIB})$$

$$= \sigma_{(100)} \left\{ \left(\frac{1-S}{2}\right) f_{IIA} + \left(\frac{1+S}{2}\right) f_{IIB} \right\}$$

$$= 2\sigma_{(100)}\delta \left\{ \frac{(1-S^2)}{2}(\xi_{AA}+\xi_{BB})+(1+S^2)\xi_{BA} \right\}.$$

This force $\mathbf{F}$ corresponds to the attractive force between two parts of an alloy divided between the neighboring (100) planes by an imaginary plane. Now the stress $\mathbf{F}$ arises in the body of the alloy due to the change from $d_{(100)}$ to $d_{(100)}+\delta$ of lattice plane spacing. From the definition of Young's modulus that $\mathbf{F}=E^{(s)}_{[100]}\dfrac{\delta}{d_{(100)}}$, Young's modulus $E^{(s)}_{[100]}$ in the state of the degree of order S with respect to the [100] direction can be easily obtained.

$$E^{(s)}_{[100]}=2\sigma_{(100)}d_{(100)}\left\{\frac{(1-S^2)}{2}(\xi_{AA}+\xi_{BB})\right.$$
$$\left. +(1+S^2)\xi_{BB}\right\} \qquad (7)$$

Owing to the uncertainty of numerical values of ξ_{AA}, etc, $E^{(s)}_{[100]}$ cannot be evaluated from the above equation. However, denoting $E^{(s)}_{[100]}$ in the state of perfect order by $E^{(1)}_{[100]}$,

$$E^{(1)}_{[100]}=4\sigma_{(100)}d_{(100)}\xi_{BA}=4N_v\,d^2_{(100)}\xi_{BA},$$

where N_v is the volume density of atoms. Accordingly,

$$E^{(s)}_{[100]}=\frac{E^{(1)}_{[100]}}{2}\left\{\frac{(1-S^2)}{2}\frac{(\xi_{AA}+\xi_{BB})}{\xi_{BA}}\right.$$
$$\left. +(1+S^2)\right\}. \qquad (8)$$

The above equation gives the relation between Young's modulus in the state of the degree of order S and that in the state of perfect order.

(ii) Young's modulus in the [110] direction

When the unit cell suffers an elongation 2δ in the [110] direction without lateral contraction, atoms on the neighboring (110) plane to the left side of the atom O which contribute to the change of potential energy of the atom O in the centre are only atoms 1 and 2.

Let the contribution from atoms 1 and 2 to the potential energy of the atom O be $\phi_{IIA}(r)$ or $\phi_{IIB}(r)$ according to the kind of the atom O, and from *Eq.* (3)

$$\phi_{IIA}(r)=\sum_{1,2}V_{IIA}(r)=\sum_{1,2}\left[(V_{IIA})^0\right.$$
$$\left.+\frac{\delta^2}{3}\left(\frac{d^2V_{IIA}}{dr^2}\right)^0\right]$$
$$=(\phi_{IIA})^0+\frac{2}{3}\delta^2\left(\frac{d^2V_{IIA}}{dr^2}\right)^0.$$

It follows,

$$f_{IIA}=-\frac{\partial\phi_{IIA}(r)}{\partial\delta}=-\frac{4}{3}\delta\left(\frac{d^2V_{IIA}}{dr^2}\right)^0$$
$$=-\frac{4}{3}\delta\left\{\frac{(1+S)}{2}\left(\frac{d^2V_{AA}}{dr^2}\right)^0\right.$$
$$\left.+\left(\frac{1-S}{2}\right)\left(\frac{d^2V_{BA}}{dr^2}\right)^0\right\}.$$

After substitution with ξ_{AA}, etc.,

$$f_{IIA}=-4\delta\left\{\left(\frac{1+S}{2}\right)\xi_{AA}+\left(\frac{1-S}{2}\right)\xi_{BA}\right\}.$$

Similarly

$$f_{IIB}=-4\delta\left\{\left(\frac{1-S}{2}\right)\xi_{BB}+\left(\frac{1+S}{2}\right)\xi_{BA}\right\}.$$

Since the (110) plane containing the atom O belongs not only to the II lattice but to the I lattice, f_{IA} and f_{IB} have also to be considered. Considering similarly, we get

$$f_{IA}=-4\delta\left\{\left(\frac{1-S}{2}\right)\xi_{AA}+\left(\frac{1+S}{2}\right)\xi_{BA}\right\}.$$

$$f_{IB}=-4\delta\left\{\left(\frac{1+S}{2}\right)\xi_{BB}+\left(\frac{1-S}{2}\right)\xi_{BA}\right\}.$$

Denoting the surface density of atoms on the (110) plane by $\sigma_{(110)}$, one half of atoms on the unit area belongs to the I lattice and another half to the II lattice, and there are $\left(\dfrac{1+S}{2}\right)\sigma_{(110)}/2$ of A atoms and $\left(\dfrac{1-S}{2}\right)\sigma_{(110)}/2$ of B atoms on I sites, and $\left(\dfrac{1-S}{2}\right)\sigma_{(100)}/2$ of A atoms and $\left(\dfrac{1+S}{2}\right)\sigma_{(110)}/2$ of B atoms on II sites.

Then the attractive force $\mathbf{F}$ between atoms on this unit area and those on the neighboring plane due to the elongation δ of lattice plane spacing, is

$$\mathbf{F} = f_{IIA}\Big(\frac{1-S}{2}\Big)\sigma_{(110)}/2 + f_{IIB}\Big(\frac{1+S}{2}\Big)\sigma_{(110)}/2$$

$$+ f_{IA}\Big(\frac{1+S}{2}\Big)\sigma_{(110)}/2 + f_{IB}\Big(\frac{1-S}{2}\Big)\sigma_{(110)}/2 .$$

$$= \frac{\sigma_{(110)} \cdot \delta}{2}\Big[\big\{(1-S)(1+S)\xi_{AA}+(1-S)^2\xi_{BA}\big\}$$

$$+ \big\{(1-S)(1+S)\xi_{BB}+(1+S)^2\xi_{BA}\big\}$$

$$+ \big\{(1-S)(1+S)\xi_{AA}+(1+S)^2\xi_{BA}\big\}$$

$$+ \big\{(1+S)(1-S)\xi_{BB}+(1-S)^2\xi_{BA}\big\}\Big]$$

$$= 2\sigma_{(110)}\delta\Big\{\frac{(1-S^2)(\xi_{AA}+\xi_{BB})}{2}+(1+S^2)\xi_{BA}\Big\} .$$

As before, from the relation

$$\mathbf{F} = E^{(s)}_{(110)}\frac{\delta}{d_{(110)}} ,$$

$$E^{(s)}_{(110)} = 2\sigma_{(110)}d_{(110)}\Big\{\frac{(1-S^2)}{2}(\xi_{AA}+\xi_{BB})$$

$$+(1+S^2)\xi_{BA}\Big\} . \tag{9}$$

Then

$$E^{(1)}_{(110)} = 4\sigma_{(110)}\,d_{(110)}\,\xi_{BA}$$

$$= 4N_v\,d^2_{(110)}\,\xi_{BA} . \tag{10}$$

Therefore we obtain,

$$E^{(s)}_{(110)} = \frac{E^{(1)}_{(110)}}{2}\Big\{\frac{(1-S^2)}{2}\frac{(\xi_{AA}+\xi_{BB})}{\xi_{BA}}$$

$$+(1+S^2)\Big\} . \tag{11}$$

Again we obtained an equation in the [110] direction as similar as *Eq.*(8).

(iii) Young's modulus in the [111] direction

Similarly as in the two cases, above described, assume that the unit cell suffers an elongation 2δ in the [111] direction without lateral contraction. In the calculation of the attractive force between the two parts of the alloy divided between the neighboring [111] planes by an imaginary plane as shown in Fig. 3, it is not sufficient to take only the force between the nearest neighboring planes into account. The spacing between the nearest neighboring (111) plane is $\frac{\sqrt{3}}{6}a$. Of the four atoms to the left side of the imaginary plane which have influence on the atom O, atoms 1, 3 and 6 lie on the first neighboring (111) plane of the (111) plane containing the atom O, and the atom 2 lies on the third neighboring (111) plane of it. Atoms on
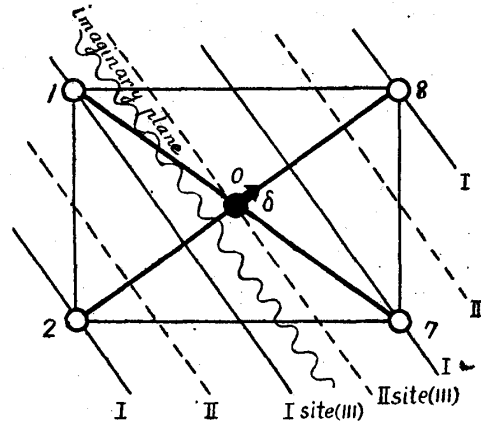

Fig. 3.   Cross section of the unit cell through the 1, 2, 7, and 8 atoms.

the second neighboring plane would exert no influence on the atom O under the nearest neighbor assumption, since they belong to the same sublattice II as does the atom O. We denote the potential energy and force which atoms 1, 3, and 6 contribute to the atom O, by ϕ_{IIA}' and f_{IIA}' respectively, and those which the atom 2 contributes to the atom O, by ϕ_{IIA}'' and f_{IIA}'', if the atom O is A atom. Similarly we define ϕ_{IIB}', f_{IIB}', ϕ_{IIB}'' and f_{IIB}''. Moreover, the atom 1 has influence on an atom in the same relative position as the atom 2 does on the atom O (which is to the same side of the imaginary plane as the atom O), and there is also an equal interaction between an atom which is on the first neighboring (111) plane to the right side of the atom 2 and an atom on the (111) plane containing the atom 7. Therefore, when we calculate the attractive force between two parts of the alloy divided between the neighboring (111) planes by an imaginary plane, we have to take three times of the values summed over an unit area in regard to f_{IIA}'' and f_{IIB}'' into account.

$$\phi_{IIA}' = (\phi_{IIA}')^0 + \Big(\frac{\delta}{3}\Big)^2\Big/2\cdot\Big\{\sum_{1,3,6}\frac{1}{9}\Big(\frac{d^2V_{IIA}}{dr^2}\Big)^0\Big\}$$

$$= (\phi_{IIA}')^0 + \Big(\frac{\delta}{3}\Big)^2\Big/2\cdot 1/3\cdot\Big(\frac{d^2V_{IIA}}{dr^2}\Big)^0 ,$$

$$\phi_{IIA}'' = (\phi_{IIA}'')^0 + \frac{\delta^2}{2}\Big(\frac{d^2V_{IIA}}{dr^2}\Big)^0 .$$

$$f_{IIA}' = -\frac{\partial\phi_{IIA}'}{\partial(\delta/3)} = -\frac{1}{3}\Big(\frac{\delta}{3}\Big)\Big(\frac{d^2V_{IIA}}{dr^2}\Big)^0$$

$$= -\frac{\delta}{9}\Big\{\Big(\frac{1+S}{2}\Big)\Big(\frac{d^2V_{AA}}{dr^2}\Big)^0$$

$$+\Big(\frac{1-S}{2}\Big)\Big(\frac{d^2V_{BA}}{dr^2}\Big)^0\Big\} .$$

$$f_{\pi A}'' = -\frac{\partial \phi_{\pi A}''}{\partial \delta} = -\delta \left(\frac{d^2 V_{\pi A}}{dr^2}\right)^0$$

$$= -\delta \left\{ \left(\frac{1+S}{2}\right)\left(\frac{d^2 V_{AA}}{dr^2}\right)^0 + \left(\frac{1-S}{2}\right)\left(\frac{d^2 V_{\pi A}}{dr^2}\right)^0 \right\}.$$

Then

$$f_{\pi A}' = -\frac{\delta}{3}\left\{ \left(\frac{1+S}{2}\right)\xi_{AA} + \left(\frac{1-S}{2}\right)\xi_{BA} \right\}.$$

$$f_{\pi A}'' = -3\delta\left\{ \left(\frac{1+S}{2}\right)\xi_{AA} + \left(\frac{1-S}{2}\right)\xi_{BA} \right\}.$$

Similarly,

$$f_{\pi B}' = -\frac{\delta}{3}\left\{ \left(\frac{1-S}{2}\right)\xi_{BB} + \left(\frac{1+S}{2}\right)\xi_{BA} \right\}.$$

$$f_{\pi B}'' = -3\delta\left\{ \left(\frac{1-S}{2}\right)\xi_{BB} + \left(\frac{1+S}{2}\right)\xi_{BA} \right\}.$$

Denoting the surface density of atoms on the (111) plane by $\sigma_{(111)}$, the unit area containing the atom O has $\left(\frac{1-S}{2}\right)\sigma_{(111)}$ of A atoms and $\left(\frac{1+S}{2}\right)\sigma_{(111)}$ of B atoms on it, since this unit area belongs to the II lattice. Then the attractive force F between the two parts of the alloy divided between the neighboring (111) planes by an imaginary plane, is

$$\mathbf{F} = \sum_{\text{unit area}} (f_{\pi A}' + 3f_{\pi A}'' + f_{\pi B}' + 3f_{\pi B}'')$$

$$= \frac{28}{3}\delta \cdot \sigma_{(111)}\left\{ \left(\frac{1+S}{2}\right)\left(\frac{1-S}{2}\right)\xi_{AA} + \left(\frac{1-S}{2}\right)^2 \xi_{BA} \right\}$$

$$+ \frac{28}{3}\delta \cdot \sigma_{(111)}\left\{ \left(\frac{1-S}{2}\right)\left(\frac{1+S}{2}\right)\xi_{BB} + \left(\frac{1+S}{2}\right)^2 \xi_{BA} \right\}$$

$$= \frac{28}{6}\delta \cdot \sigma_{(111)}\left\{ \frac{(1-S^2)}{2}(\xi_{AA} + \xi_{BB}) \right.$$

$$\left. + (1+S^2)\xi_{BA} \right\}.$$

As before, from the definition of Young's modulus $E_{(111)}^{(s)}$ that

$$\mathbf{F} = E_{(111)}^{(s)} \frac{\left(\frac{\delta}{3}\right)}{d_{(111)}},$$

$$E_{(111)}^{(s)} = \frac{28}{2}\sigma_{(111)} d_{(111)}\left\{ \frac{(1-S^2)}{2}(\xi_{AA} + \xi_{BB}) \right.$$

$$\left. + (1+S^2)\xi_{BA} \right\}. \quad (12)$$

In the state of perfect order,

$$E_{(111)}^{(1)} = 28\sigma_{(111)}d_{(111)}\xi_{BA} = 28N_v d^2_{(111)}\xi_{BA}. \quad (13)$$

Then

$$E_{(111)}^{(s)} = \frac{E_{(111)}^{(1)}}{2}\left\{ \frac{(1-S^2)(\xi_{AA} + \xi_{BB})}{2\xi_{BA}} \right.$$

$$\left. + (1+S^2) \right\}. \quad (14)$$

In this case the result is also similar to those in the former two cases.

III. Young's modulus of polycrystals

The principal elastic coefficient s_{11}, s_{11}, and s_{44} of a cubic crystal are related to Young's modulus by the formula

$$1/E = s_{11} - 2sF(l, m, n)^{(11)}, \quad (15)$$

where $s = s_{11} - s_{12} - \frac{1}{2}s_{44}$ and $F(l, m, n)$ is the orientation function. The orientation function $F(l, m, n)$ upon which Young's modulus in any direction depends is

$$F(l, m, n) = l^2 m^2 + m^2 n^2 + n^2 l^2$$

in which l, m and n are the direction cosines of the length of the specimen with respect to the crystallographic axes. Upon substitution of 1/3, 1/4 and zero, respectively, for the orientation function, Eq. (15) yields $1/E_{(111)}$, $1/E_{(110)}$ and $1/E_{(100)}(=s_{11})$. After eliminating s_{11} etc. in Eq. (15), it becomes

$$1/E = 1/E_{(100)} - 4(1/E_{(100)} - 1/E_{(110)})$$

$$\times (l^2 m^2 + m^2 n^2 + n^2 l^2). \quad (16)$$

Young's modulus of a quasi-isotropic solid can be obtained by averaging Eq. (16) with respect to the solid angle $\sin\theta d\theta d\varphi$.[12] The average value of $F(l, m, n)$ is 1/5. Then,

$$\left(\overline{\frac{1}{E}}\right) = 1/E_{(100)} - 4/5 \cdot (1/E_{(100)} - 1/E_{(110)})$$

$$= 4/5 \cdot (1/E_{(110)}) + 1/5 \cdot (1/E_{(100)}).$$

$(\overline{1/E})$ may be regarded as that of a polycrystal. Young's modulus of a polycrystal in the state of the degree of order S is

$$1/E^{(s)} = 4/5 \cdot (1/E_{(110)}^{(s)}) + 1/5 \cdot (1/E_{(100)}^{(s)}).$$

From above calculations,

$$1/E_{(110)}^{(s)} = 1/[f(s) \cdot E_{(110)}^{(1)}],$$

and $$1/E_{(100)}^{(s)} = 1/[f(s) \cdot E_{(100)}^{(1)}]$$

where

$$f(s) = 1/2 \cdot \left\{ \frac{(1-S^2)(\xi_{AA} + \xi_{BB})}{2\xi_{BA}} + (1+S^2) \right\}.$$

Accordingly,

$$E^{(s)} = f(s)E^{(1)} = \frac{E^{(1)}}{2}\left\{ \frac{(1-S^2)(\xi_{AA} + \xi_{BB})}{2\xi_{BA}} \right.$$

$$\left. + (1+S^2) \right\}. \quad (17)$$

Thus for the case of a polycrystal the same formula as that for the case of a single crystal in the three principal directions is obtained.

IV. Comparison with experiment

(i) The variation of Young's modulus with the degree of order

According to the results above obtained, Young's modulus of beta brass can be expressed by the following formula, whether it is a single crystal or a polycrystal:

$$E^{(s)} = \frac{E^{(1)}}{2}\left\{\frac{(1-S^2)(\xi_{AA}+\xi_{BB})}{2\xi_{BA}}\right.$$
$$\left.+(1+S^2)\right\}. \qquad (18)$$

Giving several values to the ratios of parameters ξ_{AA} etc. the results may be compared with those of Rinehart with respect to beta brass single crystals, and with those of Koester with respect to polycrystals (Tab. 1 (a) (b)). Tab. 1 shows Young's modulus with the values greater than $\eta=1.75$ or $\zeta=1.5$ decreases with the decreasing degree of order.

Table 1.

$E^{(s)}/E^{(1)}$ for various values of ratios of paremeters.

(a)

$\xi_{AA}:\xi_{BB}:\xi_{BA} = 2:1:\eta$	
η	$E^{(s)}/E^{(1)}$
1	$(2.5-0.5S^2)/2$
1.5	1
1.75	$(6.5+0.5S^2)/7$
2	$(7+S^2)/8$
3	$(3+S^2)/4$
4	$(11+5S^2)/16$

(b)

$\xi_{AA}:\xi_{BB}:\xi_{BA} = 1:1:\zeta$	
ζ	$E^{(s)}/E^{(1)}$
0.5	$(3-S^2)/2$
1	1
1.5	$(5+S^2)/6$
2	$(3+S^2)/4$

These values of the ratios of parameters may be appropriate to the cases of single crystals in the [110] direction and of polycrystals. Tab. 2 shows the ratios of $E^{(0)}$, Young's modulus in the state of perfect disorder (at the critical temperature for order) to $E^{(1)}$, that in the state of perfect order, and also the ratios calculated with experimental data.

Nagamiya and others[13] developed a theory of superlattice by taking atomic vibrations into account. They discussed the critical temperature for order and anomalous specific heats, giving several values to $\xi_{AA}:\xi_{BB}:\xi_{BA}$. According to it, in the case of $\eta=2$ or $\zeta=1.5$, their theory gave better agreement between theory and experiment in regard to anomalous specific heats than Bragg-Williams' or Bethe's theory. In the case of $\eta=3$ or $\zeta=2$, ΔC_v, the anomalous specific heat in the state of perfect disorder, agrees more satisfactorily with the experimental one. ξ_{AA} etc. adopted by Nagamiya are

$$\xi_{AA} = \frac{1}{3}\left(\frac{d^2V_{AA}}{dr^2}\right)^0 + \frac{1}{r_0}\left(\frac{dV_{AA}}{dr}\right)^0, \text{ etc.} \quad (19)$$

In our case the second term is vanishing. Strictly speaking, ξ_{AA} etc. in Eq.(19) are not equal to those in Eq.(6). However, at the points in the neighborhood of which V_{AA} etc. are the minimum the second term is nearly zero. In this case it may be said that our ξ_{AA} etc. in Eq.(6) are nearly equal to those in Eq.(19). Our assumption expressed in Eq.(4) does not assume that individual V_{AA} etc. are always the minimum at the equilibrium positions. If the second term in Eq.(19) is vary small, it may be regarded that our ξ_{AA} etc. are nearly equal to Nagamiya's ξ_{AA} etc. As Tab. 2 shows, Young's modulus obtained thus theoretically for the case of $\eta=2$ or $\zeta=1.5$ agrees fairly well with that obtained experimentally, and agreement is more satisfactory for the case of $\eta=3$ or $\zeta=2$. We wonder if there is some significance that both theories of anomalous specific heats and Young's modulus show good agreement with experiments for the cases of $\eta=2$ or 3 and $\zeta=1.5$ or 2. Fig. 4* shows $E^{(s)}/E^{(1)}$ as functions of

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* For $\eta=3$ or $\zeta=2$, agreement between theory and experiment is better at the critical temperature Tc, but at intermediate temperatures agreement is poor.

Table 2. Comparison of theoretical $E^{(0)}/E^{(1)}$
with experiments

η,ζ	η		ζ		Experiments	
	2	3	1.5	2	Rinehart [110]	Koester (polycrystal)
$E^{(0)}/E^{(1)}$	87.5%	75%	83.3%	75%	78.9%	70.5%

temperature for $\eta=2$ and $\zeta=1.5$, and also shows those obtained from experimental data of Rinehart with respect to the [110] direction of a single crystal and of Koester with respect to a polycrystal.

Eq. (18) shows that Young's modulus in the three principal directions [100], [110] and [111] together changes with increasing temperature as shown in Fig. 4.
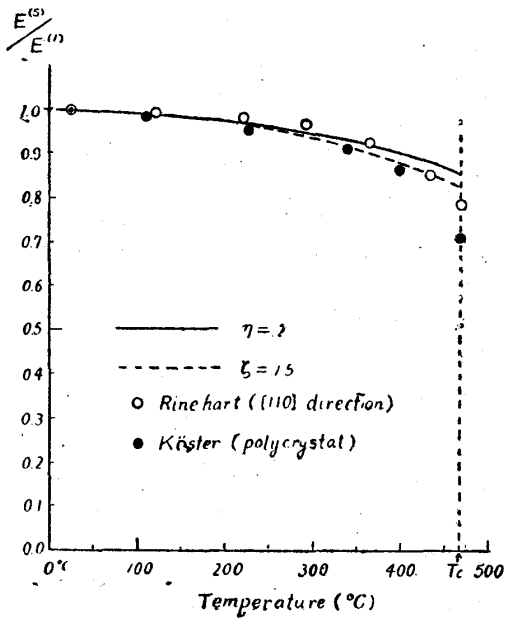

Fig. 4. The temperature variation curves
of $E^{(s)}/E^{(1)}$ for the case of $\eta=2$
and $\zeta=1.5$.

Experimental results of Rinehart, however, show that Young's modulus in the [100] direction increases with increasing temperature, reaches a maximum value and then decreases to $E^{(0)}_{(100)}$, and that Young's modulus in the [111] direction shows an appoximately linear decrease with increasing temperature to $E^{(0)}_{(111)}$. The present theory cannot explain these behaviors.

(ii) **The anisotropy of Young's modulus**
Eq. (15) shows there is a linear relation

between reciprocal of Young's modulus and the orientation function. Next we examined to what extent the present theory can explain the anisotropy of Young's modulus. From *Eqs.* (7), (8), (9), (10), (12) and (13), we get

$$\frac{1}{E^{(s)}_{(100)}} : \frac{1}{E^{(s)}_{(110)}} : \frac{1}{E^{(s)}_{(111)}} = \frac{1}{E^{(1)}_{(100)}} : \frac{1}{E^{(1)}_{(110)}} : \frac{1}{E^{(1)}_{(111)}}$$

$$=1:0.5:0.43. \qquad (20)$$

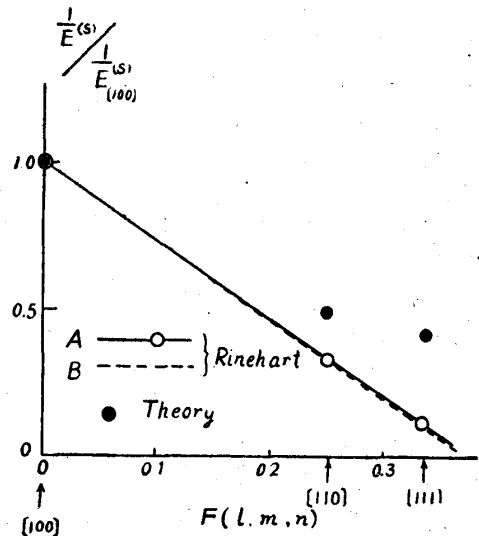Fig. 5 shows comparison of the above results with Rinehart's experimental data.

Fig. 5. $\dfrac{1}{E^{(s)}} \Big/ \dfrac{1}{E^{(s)}_{(100)}}$ against the orientation
function.
A   at room temperature.
B   at 466°C.

The results of Rinehart is quite in agreement with *Eq.* (15). Our result in the [110] direction agrees fairly well that of Rinehart, but in the [111] direction the discrepancy is somewhat large. However, it can be seen that although our result does not show a linear relation, $1/E$ decreases with increasing orientation function. *Eq.* (20) indicates that the anisotropy is independent of

temperature. Both this result and that of Rinehart as shown in Fig. 5 are contrary to the prediction of Webb[14] that the anisotropy of beta brass would decrease with increasing disorder and the alloy would become more nearly isotropic in the neighborhood of the critical temperature for order.

V. Conclusion

Although it may not be justified that the interaction between atoms in a metal or an alloy is described in terms of potential energy between two atoms, we assume this to be the case in the approximation, and moreover assume that the interatomic force acts between the nearest neighbor atoms only. With these assumptions, assuming further that a beta brass crystal lattice suffers an elongation in one of the three principal directions of crystallographic axes without lateral contraction, we obtained theoretically Young's modulus corresponding to the state of any degree of order by calculating the force between two parts of the alloy divided between the neighbor lattice planes by an imaginary plane. Now that cohesive energy of beta brass has not yet been calculated quantum-mechanically, Young's modulus thus calculated may be regarded as one of a reasonable approximation. It was shown that the theory of Young's modulus with the same values in the ratios of parameters $\xi_{AA}:\xi_{BB}:\xi_{BA}$, with which the theory of superlattice can explain more satisfactorily the anomalous specific heat of the alloy than Bragg-Williams' or Bethe's theory does, could explain qualitatively the experimental results due to Rinehart or Koester of the temperature dependence of Young's modulus and that the theory could explain also in the same degree of accuracy the results due to Rinehart in regard to the anistotropy of Young's modulus.

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