

whole composition range by assuming almost constant  $F$  and Levin *et al.*<sup>10)</sup> discussed dilute Ni region. The latter authors have pointed out the appropriateness of decreasing  $F$  with  $c$ . For Ni-Pt, on the other hand, Schindler<sup>20)</sup> has investigated on the basis of uniform enhancement model, in which Pt as well as Ni is attributable to  $T_c$  and  $U_{\text{eff}}$  may be the weighted mean with  $c$  of those of Ni and Pt. Also this alloy has been considered as homogeneous one<sup>21)</sup> and above statements may be accepted. Ni-Rh: Levin *et al.*<sup>10)</sup> have pointed that uniform enhancement model may be applied to dilute Ni region. With respect to  $F$ ,  $F(c)$  is not monotonic, but will take maximum judging from the state density of Ni and Rh,<sup>19)</sup> since Rh has one less electron than Ni.

### 3.2 Pressure effects on $T_c$ , $\Delta T_c/\Delta p$

The pressure effects on  $T_c$ ,  $\Delta T_c/\Delta p$ , obtained for the alloys are shown in Fig. 4 as a function of solute concentration  $c$ . Because  $T_c$  changed linearly with applied pressure in the pressure range presently employed,  $\Delta T_c/\Delta p$  could be determined uniquely from the slope of  $T_c$  vs pressure curve.

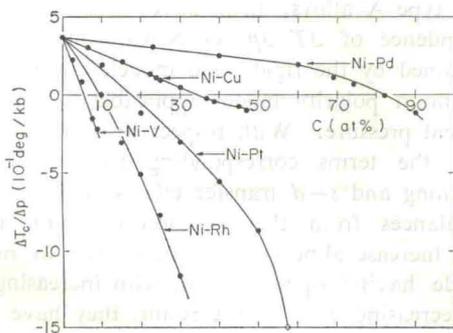


Fig. 4. A plot of the pressure effects on  $T_c$ ,  $\Delta T_c/\Delta p$ , as a function of solute concentration  $c$ .

The experimental results shown in Fig. 4 are arranged as follows: (i) For all the alloys,  $\Delta T_c/\Delta p$  decreases with increasing  $c$ . The initial rate of decrease is largest for Ni-V and smallest for Ni-Pd alloys, likewise the case of  $T_c$  at normal pressure in Fig. 3. (ii) For each alloy,  $\Delta T_c/\Delta p$  changes the sign from positive in Ni rich region to negative as  $c$  increases. The reduced solute concentrations to  $c_F$ ,  $c/c_F$ 's, where  $\Delta T_c/\Delta p$  changes the sign are about 0.3 for Ni-Pt and -Rh, 0.6 for Ni-V and -Cu, and 0.85 for Ni-Pd alloys. The data on  $\Delta T_c/\Delta p$  near  $c_F$  have been obtained for Ni-Pd by Beille<sup>22)</sup> and

-Pt by Alberts *et al.*<sup>21)</sup> and only the result for  $\text{Ni}_{42.9}\text{Pt}_{57.1}$  is plotted in Fig. 3, since the behavior near  $c_F$  is not the main object in the present work. (iii) For Ni-V and -Cu alloys,  $\Delta T_c/\Delta p$ 's change almost linear. For the others, curves are concave downward. Among them, the variation of the curve is rapid near  $c_F$  for Ni-Pt and -Rh alloys. (iv) Unlike the case at normal pressure, no coincidence of the curves has been obtained for Ni-Cu and -Pt alloys. This result suggests<sup>7)</sup> that the data on  $\Delta T_c/\Delta p$  will play a part to the classification of characteristics of alloys at normal pressure.

In the current investigation of  $\Delta T_c/\Delta p$  derived from  $T_c$  in eq. (1), the following conditions have been assumed: (i) The band width  $W$  of the  $d$ -band depends on the Heine's relation,<sup>23)</sup>  $W \propto R^{-5}$ , where  $R$  is the interatomic distance. (ii) The  $d$ -band is widened uniformly with pressure. (iii) The effective correlation energy  $U_{\text{eff}}$  employed is the Kanamori type<sup>24)</sup>

$$U_{\text{eff}} = \frac{U_b}{1 + U_b K}, \quad (2)$$

where  $U_b$  is coulomb self-energy of an atomic orbital and  $K$  is a quantity depending on the band shape.

Besides these assumptions proposed by L.E. for the analysis of  $\Delta T_c/\Delta p$  of Ni and Ni-Cu alloys, L.E. have also introduced the compression-induced conduction band effect ( $s$ - $d$  transfer). The expression for  $\Delta T_c/\Delta p$  derived by them is

$$\frac{dT_c}{dp} = \frac{5}{3} \kappa T_c + (\xi_1' + \xi_2 + \xi_3) \frac{5}{3} \kappa T_c, \quad (3)$$

where  $\kappa$  is the volume compressibility of the material. In eq. (3), the 1st term  $(5/3)\kappa T_c$  corresponds to a simple case of  $d$ -band widening in which  $U_{\text{eff}}$  is infinite and the effect of  $s$ -band is neglected. The term  $\xi_1'$  is the contribution of the  $d$ -band in case of  $U_{\text{eff}}$  being finite, referred to as  $d$ -band widening in the present paper, and  $\xi_2 + \xi_3$  come from the  $s$ - $d$  transfer with compression. The term  $\xi_2$  in eq. (3), however, has not been considered here, since L.E. have pointed that this term is never of primary importance.

Comparing eq. (3) with the expression obtained by Shiga,<sup>4)</sup> who has investigated  $\Delta T_c/\Delta p$  of Invars without considering  $s$ - $d$  transfer, eq. (3) can be written as

$$\frac{dT_c}{dp} = \frac{5}{3} \kappa T_c + \frac{D}{T_c} \quad (4a)$$

$$D = \frac{\kappa}{2k^2\alpha} \left[ -\frac{5}{3} \frac{U_{\text{eff}}}{U_b} + \frac{N_c}{\tilde{F} + F_c} \left( \frac{F_s}{F} - K_s U_{\text{eff}} \right) 0.36 \right], \quad (4b)$$

where  $k$  is the Boltzmann's constant and notations  $N_c$ ,  $F_c$ ,  $F_s$ ,  $\tilde{F}$  and  $K_s$  are referred to the article of L.E., and  $\alpha$  to Shiga. It is understandable that (i) from eq. (4a),  $\Delta T_c/\Delta p$  consists of two terms which are proportional and inversely proportional to  $T_c$  at first sight, (ii) in eq. (4b), the 1st and 2nd terms in the brackets in  $D$  are functions of  $F$  and  $U_b$  or  $F$  and  $U_{\text{eff}}$ , where  $K$  acts through  $F$ , and correspond to  $\xi_1'$  ( $d$ -band widening) and  $\xi_s$  ( $s$ - $d$  transfer) terms in eq. (3), respectively. Shiga's expression is the sum of  $(5/3)\kappa T_c$  and the 1st term in  $D$ .

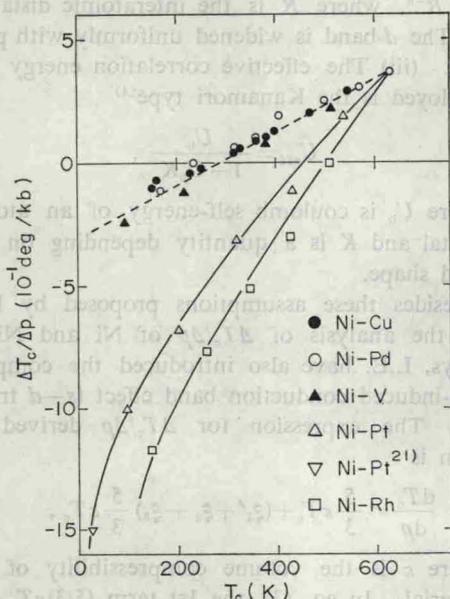


Fig. 5. A plot of  $\Delta T_c/\Delta p$  as a function of  $T_c$ .

On the basis of considerations mentioned above, results for  $\Delta T_c/\Delta p$  plotting as a function of  $T_c$  will bear a rather profound meaning than plotting as a function of  $c$  such as shown in Fig. 4. Figure 5 thus shows  $\Delta T_c/\Delta p$  as a function of  $T_c$ . It is to be noted that the functional forms of  $\Delta T_c/\Delta p$  in Fig. 5 are classified into two types, A and B. In type A, the linearity of  $\Delta T_c/\Delta p$  with  $T_c$  almost holds. Ni-V, -Cu and -Pd alloys belong to this type and the data almost lie on a line expressed as  $\Delta T_c/\Delta p = (5/3)\kappa T_c - 3 \times 10^{-1}$  in unit of deg/kb, using the compressibility  $\kappa$  of Ni at room temperature.<sup>26)</sup> The concentration and temperature dependence

of  $\kappa$  for the alloys may be neglected for the present purpose, judging from the experimental results.<sup>26, 26)</sup> For Ni-Pd, the deviation from the linearity near  $c_F$  has been reported,<sup>22)</sup> but the behavior near  $c_F$  is not the main object in the present paper as is mentioned above. In type B alloys, on the other hand,  $\Delta T_c/\Delta p$  vs  $T_c$  curve is not linear, concave downward from Ni rich side. Ni-Pt and -Rh alloys belong to this type. In other words, type A or B is that in which the 2nd term  $D/T_c$  in eq. (4a) is constant independent of  $T_c$  or  $c$ , or a function of  $T_c$  or of  $c$ .

These results will be discussed qualitatively on the basis of the following standpoints: (i) The discrimination between type A and type B might be made essentially from the dependence of  $F$  and  $U_b$  on  $T_c$  or from the degree of contribution of the  $d$ -band widening and the  $s$ - $d$  transfer effects to  $D$ . (ii) The results obtained by Lang<sup>27)</sup> and L.E. that  $D$  shifts to the negative side regardless of its sign when  $F$  and  $U_b$  decreases, may be accepted as general tendency and applied to the alloys presently concerned, as far as discussions will be made from eq. (4a) and (4b).

In type A alloys, L.E. have pointed that  $c$  dependence of  $\Delta T_c/\Delta p$  for Ni-Cu could not be explained by the rigid band model, but by the minimum polarity model applicable to  $T_c(c)$  at normal pressure. With respect to  $D/T_c$  in eq. (4b), the terms corresponding to the  $d$ -band widening and  $s$ - $d$  transfer effects almost counterbalances from their numerical results that they increase almost in the same way in magnitude having opposite sign, with increasing  $c$ , or decreasing  $T_c$ . As the result, they have obtained constant  $D/T_c$ .

Above mentioned results for Ni-Cu obtained by L.E. could not be applied unconditionally to Ni-V and -Pd alloys belonging to type A, since the appropriate models and the detailed band shapes etc. are necessary to the final estimation. However, since the situation of  $F(c)$  and  $U_{\text{eff}}(c)$  for Ni-V would be similar to Ni-Cu as described in § 3.1, the competition between the widening and the transfer terms in Ni-V would vary as  $c$  in a similar way to Ni-Cu. On the other hand, the simple argument unlikely explain the data on Ni-Pd, but the experimental results will support the similar situation.

For type B alloys, the competition between the widening and the transfer in  $D/T_c$  should