

whole composition range by assuming almost constant F and Levin *et al.*¹⁹⁾ discussed dilute Ni region. The latter authors have pointed out the appropriateness of decreasing F with c . For Ni-Pt, on the other hand, Schindler²⁰⁾ has investigated on the basis of uniform enhancement model, in which Pt as well as Ni is attributable to T_c and U_{eff} may be the weighted mean with c of those of Ni and Pt. Also this alloy has been considered as homogeneous one²¹⁾ and above statements may be accepted. Ni-Rh: Levin *et al.*¹⁹⁾ 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,¹⁹⁾ 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.

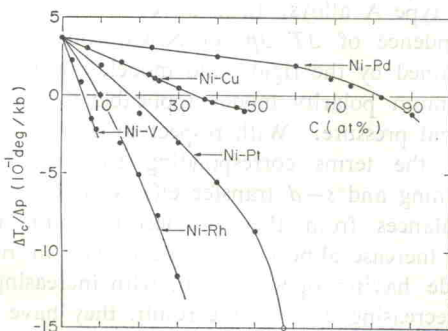


Fig. 4. A plot of the pressure effects on T_c , $\Delta T_c/\Delta p$, as a function of solute concentration c .

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 Beille²²⁾ and

-Pt by Alberts *et al.*²¹⁾ 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 suggests⁷⁾ 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,²³⁾ $W \propto R^{-5}$, where R is the interatomic distance. (ii) The d -band is widened uniformly with pressure. (iii) The effective correlation energy U_{eff} employed is the Kanamori type²⁴⁾

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

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 κ 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_{eff} is infinite and the effect of s -band is neglected. The term ξ_1' is the contribution of the d -band in case of U_{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 ξ_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,⁴⁾ who has investigated $\Delta T_c/\Delta p$ of Invars without considering $s-d$ transfer, eq. (3) can be written as

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

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

where k is the Boltzmann's constant and notations N_c , F_c , F_c , \tilde{F} and K_c are referred to the article of L.E., and α 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_{eff} , where K acts through F , and correspond to ξ_1' (d -band widening) and ξ_3 (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 .

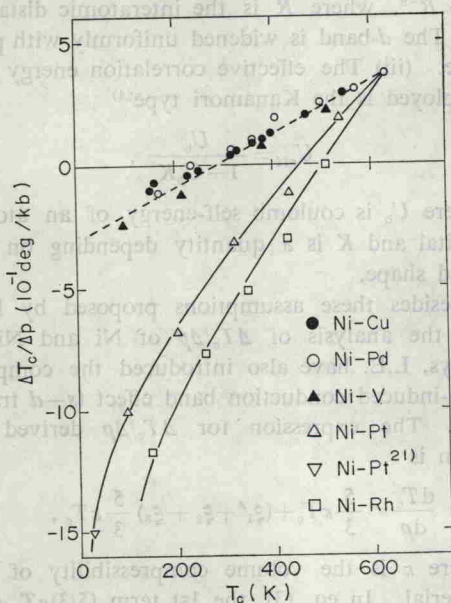


Fig. 5. A plot of $\Delta T_c/\Delta p$ as a function of T_c .

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 κ of Ni at room temperature.²⁵⁾ The concentration and temperature dependence

of κ for the alloys may be neglected for the present purpose, judging from the experimental results.^{25,26)} For Ni-Pd, the deviation from the linearity near c_F has been reported,²²⁾ 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 Lang²⁷⁾ 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