

Finally, we assume the volume dependence of  $W$  is given by Heine's<sup>23</sup> results

$$\frac{\partial \ln W}{\partial \ln V} = -\frac{5}{3} \quad (5)$$

Using the above results, Eqs. (3)–(5), the volume dependence of  $\bar{I}$ , Eq. (2), is<sup>12</sup>

$$\frac{\partial \ln \bar{I}}{\partial \ln V} = \frac{5}{3} \frac{I}{I_b}, \quad (6)$$

which is independent of  $\beta$  and  $\gamma$  and where here  $I_b$  is assumed independent of volume. For the density of states of the form given by Eq. (4), it can be shown that  $T_F \sim W$ , and hence from Eq. (5),  $\partial \ln T_F / \partial \ln V = -\frac{5}{3}$ . Using Eqs. (1), (2), (5), and (6) the volume dependence of  $T_c$  becomes

$$\begin{aligned} \frac{\partial \ln T_c}{\partial \ln V} &= \Gamma \\ &= -\frac{5}{3} + \frac{5}{6} (\bar{I} - 1)^{-1} (I/I_b). \end{aligned} \quad (7)$$

In terms of pressure, Eq. (7) can be written as

$$\frac{\partial T_c}{\partial P} = \frac{5}{3} \kappa T_c - \frac{5}{6} \kappa \frac{I}{I_b} \frac{T_F^2}{T_c}, \quad (8)$$

where  $\kappa$  is the volume compressibility and we have used Eq. (1).

We shall now show how pressure measurements of  $T_c$  can be used to determine a maximum value for  $\bar{I}$  and a minimum value for  $T_F$ . The maximum value that  $I$  can have is the bare exchange value  $I_b$ ; thus, the maximum value for the ratio  $I/I_b$  is one. Hence, the experimental value of  $\Gamma$  can be used to determine the maximum values of  $\bar{I}$ . From Eq. (7) we have

$$\bar{I}_{\max} = 1 + \frac{5}{6} \left( \Gamma + \frac{5}{3} \right)^{-1}. \quad (9)$$

Then using values for  $\bar{I}$  obtained from Eq. (9) we can obtain a minimum value for  $T_F$  using Eq. (1).

For weak itinerant-electron FM's  $\bar{I} > 1.0$  and for weak electron-correlation effects  $I/I_b \approx 1.0$ , the second term in Eq. (7) is dominant, and from Eq. (8) we have  $\partial T_c / \partial P \sim -1/T_c$ . Examples of weak itinerant-electron FM's are the Fe-Ni, Fe-Pt, and Fe-Pd Invar alloys where it has been experimentally observed that  $\partial T_c / \partial P \approx -\text{const}/T_c$ .<sup>24</sup> For strong itinerant-electron FM's  $\bar{I} > 1$  and for strong correlation effects  $I/I_b < 1$  such that the first term in Eq. (7) is dominant, and from Eq. (8) we have  $\partial T_c / \partial P \sim T_c$ . An example of a strong itinerant-electron FM is Ni, where it is found that  $\partial T_c / \partial P = \frac{5}{3} \kappa T_c \approx 0.68 \text{ }^\circ\text{K/kbar}$  in good agreement with experimental values of  $0.32\text{--}0.42 \text{ }^\circ\text{K/kbar}$ .<sup>9</sup> It is noteworthy that in the limit of weak itinerant-electron FM and for large  $\Gamma$  such that  $|\Gamma| \gg \frac{5}{3}$  and neglecting the volume dependence of  $I_b$ , the results of this paper reduce to the results given previously by Wohlfarth and Bartel.<sup>12</sup>

The localized and the itinerant, or collective,

descriptions of magnetic electrons have been investigated by Goodenough.<sup>25</sup> He considered the case of one  $d$  electron per relevant  $d$  orbital which corresponds to a half-filled band or to a half-filled localized orbital, and the magnetic order is antiferromagnetic (AFM). In the absence of competing exchange interactions, the Néel temperature  $T_N$  for localized-electron AFM increases with the transfer integral  $b$  since the exchange interaction is proportional to  $b^2$ ; whereas, it has been shown that  $T_N$  for a band AFM decreases with increasing bandwidth<sup>25,26</sup> where the bandwidth is proportional to  $b$ . Goodenough concludes that the magnetic moment and  $T_N$  should vary continuously in going from a localized to a band description. We expect  $b$  to increase with increasing pressure; hence, we expect that for the localized electron description  $T_N$  should increase with increasing pressure, and for the itinerant description  $T_N$  should decrease with increasing pressure.<sup>26</sup> Furthermore, we expect that the general arguments for an AFM apply to the FM case of interest here. The observed decrease in the FM-to-PM transition temperature in the  $\text{MnAs}_x\text{Sb}_{1-x}$  compounds suggests that the itinerant-electron description is the appropriate one. Although these compounds are anisotropic, the isotropic model discussed in this paper describes the pressure effects quite well.

## 2. Analysis of Experimental Results

In Fig. 6,  $\partial T_c / \partial P$  is plotted as a function of  $T_c$  for the  $\text{MnAs}_x\text{Sb}_{1-x}$  solid solutions in the concentration range  $0 \leq x \leq 0.8$ . For comparison, the Fe-Ni, Fe-Pd, and Fe-Pt Invar alloy data of Wayne and Bartel<sup>24</sup> are included. Similar to the Invar alloys, we observe a  $T_c^{-1}$  type of behavior as predicted by Eq. (8) when the second term in Eq. (8) dominates.

The volume derivative of  $T_c$  is calculated from  $\partial T_c / \partial P$  where the compressibility for the solid solutions was obtained by a linear extrapolation between the values of  $(2.5 \pm 0.5) \times 10^{-3} \text{ kbar}^{-1}$  for MnSb<sup>27</sup> and  $4.55 \times 10^{-3} \text{ kbar}^{-1}$  for MnAs.<sup>1</sup> The values for  $\Gamma$  are given in Table I. We observe that the values of  $\Gamma$  increase with increasing As concentration and that the magnitude of  $\Gamma$  is of the same order of magnitude as the first term in Eq. (7). In previous works on the Invar alloys<sup>11,12</sup> and  $\text{ZrZn}_2$ ,<sup>9-12</sup> it was observed that  $\Gamma \gg \frac{5}{3}$  and so the first term of Eq. (7) could be neglected. In the case of the  $\text{MnAs}_x\text{Sb}_{1-x}$  solid solutions, this factor of  $\frac{5}{3}$  must be included in any calculation of band parameters.

In Table I, we give the results of the calculation of  $\bar{I}_{\max}$  from Eq. (9) for the solid solutions  $0 \leq x \leq 0.80$ . The quoted error in the compressibility for MnSb will introduce an uncertainty of  $\pm 0.03$  in the value for  $\bar{I}_{\max}$ . We observe that  $\bar{I}_{\max}$  decreases with increasing As concentration. According to Wohl-

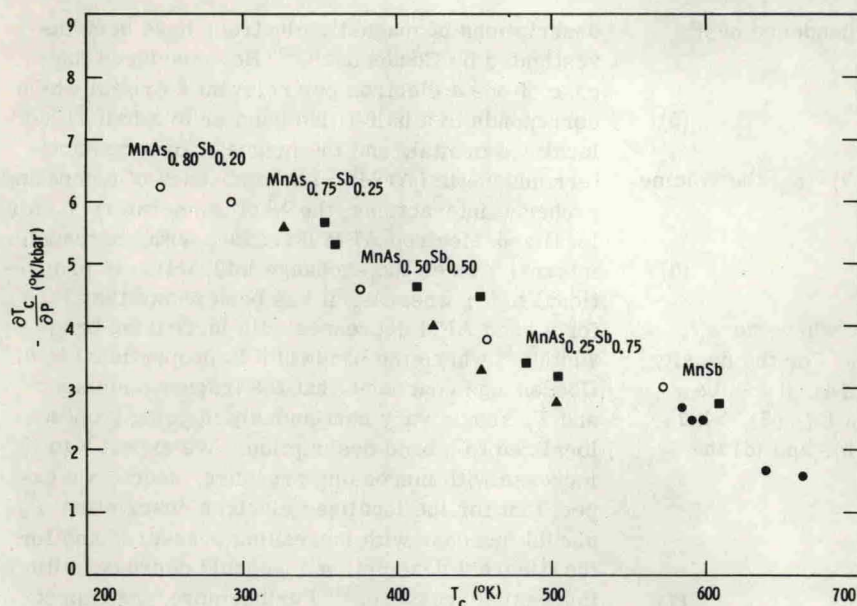


FIG. 6. A comparison of  $\partial T_c/\partial P$ -vs- $T_c$  plots for various alloy systems. Open circle,  $\text{MnAs}_x\text{Sb}_{1-x}$ ; triangles Fe-Pt; solid circle, Fe-Pd; and square, Fe-Ni.

farth's<sup>28</sup> classification, these values of  $\bar{I}_{\max}$  indicate that MnSb is approaching a strong itinerant FM, and the solid solutions are becoming weaker itinerant FM's with increasing As concentration. These values of  $\bar{I}_{\max}$  for the  $\text{MnAs}_x\text{Sb}_{1-x}$  solid solutions are comparable with the values for the Invar alloys.<sup>29</sup>

From Eq. (1), and using the value of  $\bar{I}$  and  $T_c$  for MnSb from Table I, we calculate  $T_F = 1380^\circ\text{K}$ . Thus for MnSb we see that  $T_c \approx 0.4T_F$  which indicates the Sommerfeld expansion is converging; however, the convergence is slower than one would desire. For the materials with  $x > 0$ , the convergence is more rapid than for  $x = 0$ .

Using Eqs. (1)–(4), we can express  $T_c$  as a function of the bandwidth  $W$  where we assume  $T_F \sim W$ . Then using the value of  $T_c = 572^\circ\text{K}$  and the value of  $\bar{I}_{\max}$  from Table I for MnSb, we can calculate  $T_c$  as a function of  $W$ . The results of these calculations are shown in Fig. 7. These results are independent of the value of  $I/I_b$ ,<sup>30</sup> but do not include effects of any volume dependence of  $I_b$ . Note the critical bandwidth such that for  $W/W_0 \geq 1.206$  we do not have FM order, and note the quadratic dependence of  $T_c$  on  $W$  for  $W/W_0 < 1.206$ . Using the available x-ray data<sup>31</sup> to estimate  $W/W_0$  and using the experimental values for  $T_c$  we show, in Fig. 7, the experimental results of  $T_c$  as a function of  $W/W_0$ . For  $x = 0.25$  we calculate  $T_c = 474^\circ\text{K}$  and  $\bar{I} = 1.110$  in fair agreement with the experimental values. For the solid solutions  $x > 0.25$  the agreement is only qualitative. This disagreement is not too surprising because of the large differences in unit-cell volumes for the various compositions. For these large volume differences one might expect

significant changes in the crystal-field splittings, and consequently significant changes in the electronic wave functions. Any volume dependence of  $I_b$  would modify the results shown in Fig. 7. Lacking specific-heat, susceptibility, and magnetostriction data for these materials, we cannot determine  $N(\epsilon_F)$ ,  $I$ ,  $I_b$ , and any volume dependence of  $I_b$  individually. In addition, as we shall point out below, we expect rather large electron-lattice and exchange-striction interactions for these materials, particularly for the solid solutions  $x \geq 0.80$ . Electron-lattice and exchange-striction effects have not been included in the calculations displayed in Fig. 7.

Sirota and Vasilev<sup>4</sup> have observed a Curie-Weiss type of behavior in the PM region for MnSb, with a Curie constant,  $C_M = 1.3 \text{ emu mole}^{-1} \text{ Oe}^{-1} \text{ }^\circ\text{K}^{-1}$ . According to the itinerant FM model of Wohlfarth<sup>9</sup> the susceptibility in the temperature region  $T_F \gg T > T_c$  and for  $T - T_c$  can be written as  $\chi \approx \chi_0 T_c \times (T - T_c)^{-1}$  which is a Curie-Weiss type of behavior where the Curie constant  $C_M$  is given by  $C_M = \chi_0 T_c$ . The quantity  $\chi_0$  is proportional to  $N(\epsilon_F)(\bar{I} - 1)^{-1}$ .<sup>9</sup> For MnSb,  $\chi_0$  can be calculated to give  $\chi_0 = 0.227$

TABLE I. Curie temperature  $T_c$ ,  $\Gamma \equiv \partial \ln T_c / \partial \ln V$ , and  $\bar{I}_{\max}$ , as calculated from Eq. (9), for various solid solutions of  $\text{MnAs}_x\text{Sb}_{1-x}$  in the second-order region.

$x$ (at. % As)	$T_c$	$\Gamma$	$\bar{I}_{\max}$
0.00	572	2.38	1.206
0.25	458	2.97	1.180
0.50	375	3.63	1.157
0.75	292	5.18	1.122
0.80	247	6.20	1.106