



FIG. 7. A comparison of the calculated and experimental dependence of T_c on bandwidth, solid line, calculated; solid circle, experimental.

$\times 10^{-2}$ emu mole $^{-1}$ Oe $^{-1}$ as compared to $\chi_0 = 1.38 \times 10^{-2}$ emu mole $^{-1}$ Oe $^{-1}$ for ZrZn_2 .¹⁴ This difference in χ_0 between MnSb and ZrZn_2 is consistent with the values of \bar{I} for these materials. For ZrZn_2 ,⁹ $\bar{I} = 1.0042$ and from this work for MnSb, $\bar{I}_{\text{max}} = 1.206$; thus χ_0 for MnSb should be smaller. A detailed comparison,³² however, can only be made if $N(\epsilon_F)$ for MnSb were known. For $x > 0$, χ_0 cannot be reliably extracted from the experimental data because the susceptibility has a complicated temperature dependence⁴ which is thought to be due to exchange-striction effects.

B. First-Order Region

Previous experimental studies⁶ on MnAs and $\text{MnAs}_x\text{P}_{1-x}$ have established that a first-order, hexagonal-FM-to-orthorhombic-PM, transition occurs only if the molar volume at T_c lies within a narrow critical range $V_t - \Delta V < V < V_t$, where $\Delta V/V \approx 0.025$. This narrow molar-volume range is related through the thermal expansion to the temperature range $T_t - 125^\circ\text{K} < T < T_t$, where T_t is the second-order, orthorhombic-PM-to-hexagonal-PM, transition temperature. This, coupled with the fact that there is a low-spin \rightleftharpoons high-spin transition in this temperature interval, led Goodenough and Kafalas⁶ to postulate the existence of a maximum critical bandwidth that would support spontaneous FM and the existence of a volume-dependent intra-atomic exchange interaction. This model predicts the existence of a critical pressure P_c above which the PM orthorhombic phase is stabilized to absolute zero; a $P_c = 4$ kbar has been found for MnAs.^{1,6} If P is substituted for As, then one expects P_c to decrease since the substitution of P decreases the lattice parameters (the molar volume), and thus the band-

width increases. Furthermore, if sufficient P is substituted for As, $P_c \rightarrow 0$. These effects have been observed.^{5,6} However, if Sb is substituted for As, the lattice parameters (molar volume) increase and the bandwidth decreases. Therefore, the substitution of Sb should cause P_c to increase, which is in accord with our experimental results.

Now if more than 10% Sb is substituted for As, then the molar volume will be larger than the critical volume required for a first-order transition, and the resulting solid solutions exhibit second-order transitions. If this model is correct, then at sufficiently high pressure one might expect to induce a first-order phase change in the materials with concentration $x \lesssim 0.9$. At the time this work was done, the pressures available to us (~ 4 kbar) were insufficient to check conclusively this prediction on the $x = 0.88$ solid solution. Estimations based on the isotropic Bean-Rodbell model¹⁷ indicate a second- to first-order transition pressure of approximately 16 kbar for this material. This number must be taken lightly, however, since there have been objections to using the Bean-Rodbell model in its isotropic form for MnAs.¹ We are planning to continue the search for a second- to first-order transition pressure at higher pressure in the solid solutions with concentrations $x \lesssim 0.9$.

The Bean-Rodbell model,¹⁷ which is based on a localized spin picture, has been used to describe qualitatively the first-order nature of the transition in MnAs. A similar situation arises in the itinerant electron model when the exchange and electron-lattice forces are balanced against the elastic forces. The result of this balance is that the bandwidth and exchange interaction become temperature dependent; then, depending on the parameters, the transition may tend to sharpen and may become first-order as in the Bean-Rodbell model. This type of procedure has been used to explain thermal expansion effects in an itinerant-electron AFM²⁶ where only the electron-lattice interaction was considered. In this case it was demonstrated that the balance set up between the elastic and electron-lattice forces is important in explaining the anomalous behavior of the thermal expansion for temperatures near T_N . However, for the parameters used in the theory, no first-order nature was observed in the phase transition.²⁶ It is anticipated that inclusion of exchange-striction effects could precipitate a first-order phase transition for the itinerant-electron AFM.

Unpublished x-ray data by Goodenough³³ on $\text{MnAs}_{0.80}\text{Sb}_{0.02}$ show that the unit-cell volume is quite temperature dependent for temperatures near T_c where the volume decreases continuously from a value of 70.81 \AA^3 at a temperature of approximately 100°K below T_c to a value of approximately 70.19 \AA^3 at T_c . This represents approximately 0.9% decrease

in the volume. For MnAs there is approximately a 1.8% discontinuous volume decrease at T_c for increasing temperature. It is therefore apparent that for $x \gtrsim 0.80$ there are large interactions of the lattice with the exchange energy and/or the electronic energy. The volume changes associated with these interactions depend on the magnetization. Because of the coupling, a discontinuous change in the unit-cell volume is reflected in a discontinuous change in the magnetization, and vice versa.

The physical picture we have for the results of the coupling of the magnetization and the lattice is as follows. At low temperature the magnetization takes on its saturation value, and the magnetic characteristics are determined by the bandwidth W , density of states $N(\epsilon_F)$, and the exchange interaction I . As the temperature is increased the lattice expands, and because of electron-lattice coupling and exchange striction, W decreases and I can either increase or decrease depending on the sign of $\partial \ln I / \partial \ln V$. For the material under consideration here, as W decreases, T_c will increase and the magnetization for $T < T_c$ will increase over the value it would have had if W and I did not depend on the volume. However, because of the electron-lattice and exchange-striction effects, the lattice contracts for $T \lesssim T_c$ and thus W increases and T_c decreases. Hence depending upon the amount of coupling, the rate at which W increases (or the apparent T_c decreases) determines whether the transition will be second or first order. For the first-order transition, in the words of Bean and Rodbell,¹⁷ "... this situation is like that of a man who has run beyond the brink of a cliff; there is no

gentle way down." The critical volume discussed by Goodenough and Kafalas⁶ appears to be intimately related to the electron-lattice and exchange-striction effects as a detailed theory should show.

Finally, the rather large changes in T_c with pressure for the first-order region are noteworthy. As shown in Fig. 4, there is a discontinuous change in $\partial T_c / \partial P$ at the composition which demarcates the boundary between the first- and second-order regions. In addition, there are strong hysteresis effects in the first-order region. At this time, we can offer no concrete explanation of the rather large $(\partial T_c / \partial P)$'s for the first-order region except to say that the large pressure effects appear to be connected to a "critical volume"⁶ and consequently to the electron-lattice and exchange-striction effects.

We conclude that for the first-order region electron-lattice and exchange-striction effects are important, and that inclusion of these effects in an itinerant-electron FM model (which is in a similar spirit to the Bean-Rodbell model) will be able to explain in some detail the magnetic and structural behavior. We also conclude that although the itinerant model used to discuss the second-order region is rather simple, it contains in it the essential features of a more elaborate treatment.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. G. A. Samara for useful discussions, Dr. J. B. Goodenough for his x-ray data on the $x = 0.80$ solid solution, and J. D. Pierce for expert technical assistance.

*Work supported by the U. S. Atomic Energy Commission.

¹N. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, *Phys. Rev.* **177**, 942 (1969).

²R. H. Wilson and J. S. Kasper, *Acta Cryst.* **17**, 95 (1964).

³W. Köster and E. Braun, *Ann. Phys. (Leipzig)* **4**, 66 (1959).

⁴N. N. Sirota and E. A. Vasilev, *Phys. Status Solidi* **28**, K175 (1968).

⁵J. B. Goodenough, D. H. Ridgley, and W. A. Newman, in *Proceedings of the International Conference on Magnetism, Nottingham*, 1964 (The Institute of Physics and the Physical Society, London, 1965).

⁶J. B. Goodenough and J. A. Kafalas, *Phys. Rev.* **157**, 389 (1967).

⁷J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).

⁸There must be $3d$ itinerant-electron states to account for the metalliclike electrical conductivity as observed in MnAs and MnSb [G. Fischer and W. B. Pearson, *Can. J. Phys.* **36**, 1010 (1958)] and in $(\text{Cr}_x\text{Mn}_{1-x})\text{Sb}$ [T. Suzuoka, *J. Phys. Soc. Japan* **12**, 1344 (1957)].

⁹E. P. Wohlfarth, *J. Appl. Phys.* **39**, 1061 (1968); *J. Phys. C* **2**, 68 (1969).

¹⁰D. M. Edwards and E. P. Wohlfarth, *Proc. Roy. Soc. (London)* **A303**, 127 (1968).

¹¹J. Mathon and E. P. Wohlfarth, *Phys. Status Solidi* **30**, K131 (1968); E. P. Wohlfarth, *Phys. Letters* **28A**, 569 (1969); **31A**, 525 (1970).

¹²E. P. Wohlfarth and L. C. Bartel, *Phys. Letters* **34A**, 303 (1971).

¹³G. A. Samara and A. A. Giardini, *Rev. Sci. Instr.* **36**, 108 (1965).

¹⁴R. C. Wayne and L. R. Edwards, *Phys. Rev.* **188**, 1042 (1969).

¹⁵J. E. Schirber, *Cryogenics* **10**, 418 (1970).

¹⁶T. Hirone, T. Kaneko, and K. Kondo, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrich (Academic, New York, 1965), p. 298.

¹⁷C. P. Bean and D. S. Rodbell, *Phys. Rev.* **126**, 104 (1962).

¹⁸M. Shiga, *Solid State Commun.* **7**, 559 (1969).

¹⁹The factor \bar{I} in the denominator of Eq. (1) does not appear in the previous work.

²⁰N. D. Lang and H. Ehrenreich, *Phys. Rev.* **168**, 605 (1968).

²¹J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **30**, 275 (1963).

²²If s - d overlap is a strong function of interatomic distance