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Effect of Pressure on the Ferromagnetic Transition of $MnAs_xSb_{1-x}$ Solid Solutions*

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The ferromagnetic transition temperatures of $MnAs_xSb_{1-x}$ solid solutions for $0 \leq x \leq 1$ have been measured as a function of pressure up to 4.5 kbar. Previous work has shown that for the solid solutions in the concentration range $0.9 \lesssim x \leq 1$ the magnetic transition is first order and is accompanied by a hexagonal-to-orthorhombic structure transformation, while for $0 \leq x \lesssim 0.9$ the magnetic transition is second order with no structural change. We have found that the initial pressure derivative of the transition temperature $(\partial T_c/\partial P)$ changes discontinuously in the narrow concentration range $0.87 \lesssim x \leq 0.90$, further demarcating the first- and second-order regions. We also find that substituting Sb for As in the first-order region increases the critical pressure P_c which stabilizes the orthorhombic phase to the lowest temperature. This further supports Goodenough's observation of a critical molar-volume range in which the first-order transformation occurs. The solid solutions which exhibit second-order behavior are analyzed using an itinerant-electron ferromagnet model.

I. INTRODUCTION

The isomorphic metallic compounds MnAs and MnSb have different magnetic properties which are believed to be due to differences in the Mn-Mn separation distance. For increasing temperature, MnAs exhibits a first-order ferromagnetic (FM) to paramagnetic (PM) transition at 313 °K which is accompanied by a change in crystal symmetry from the hexagonal NiAs structure ($B8_1$) to the orthorhombic MnP structure ($B31$). (Hereinafter we use FM to denote ferromagnetic, ferromagnet, or ferromagnetism, and similarly for PM.) On further heating, a second-order transition involving a change from a low-spin PM to a high-spin PM phase and a change in crystal symmetry from the orthorhombic ($B31$) to hexagonal structure[1] ($B8_1$) is observed at 398 °K. On the other hand, MnSb has a second-order FM to PM transition at 572 °K with the crystal structure remaining hexagonal ($B8_1$) through the transition.[2] A complete series of solid solutions is formed by MnAs and MnSb in which the hexagonal lattice parameters decrease monotonically from MnSb to MnAs.[3]

The various magnetic transition temperatures and crystal structures of the solid solutions, $MnAs_xSb_{1-x}$ as reported by Sirota and Vasilev[4] and Goodenough *et al.*[5] are summarized in Fig. 1. Here, for increasing temperature, T_c denotes the FM-to-PM transition temperature, T' denotes the PM-to-PM transition temperature at which the effective moment decreases, and T_t is a PM-to-PM transition temperature at which the effective moment increases and the crystal structure changes

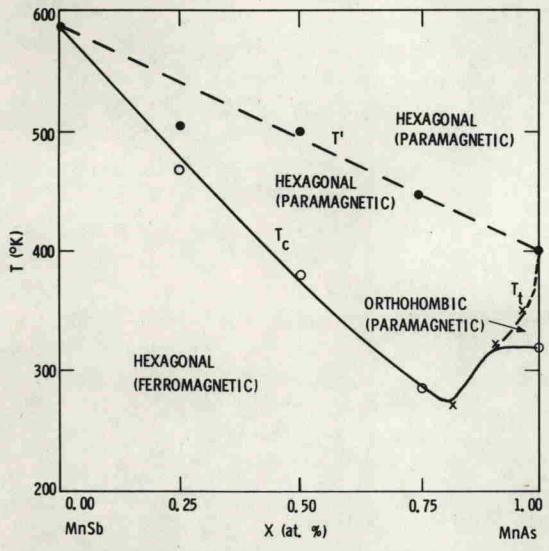

FIG. 1. Magnetic transition temperatures of $MnAs_xSb_{1-x}$ solid solutions. Open circle, solid circle after Sirota and Vasilev (Ref. 4) and × after Goodenough *et al.* (Ref. 5).

from orthorhombic to hexagonal. For the solid solutions in the concentration range $0.9 \leq x \leq 1.0$ the transition from the FM hexagonal phase to the PM orthorhombic phase is first-order. All other transitions are second order.

From Fig. 1 we see that over the concentration range $0 \leq x \leq 0.80$ the FM-to-PM transition temperature T_c decreases with increasing As concentration. In addition, the effect of substituting As for Sb is to decrease the lattice parameters[3] (decrease the Mn-Mn separation distance); thus one might expect T_c to be quite sensitive to pressure and to decrease with the application of pressure. As we shall report in Sec. II, we have observed a decrease in T_c with increasing pressure for solid solutions in this concentration range.

Goodenough and co-workers have proposed a band model to explain some of the magnetic properties of MnAs.[1,5,6] The essential features of their model are a filled s-p bonding (valence) band and an empty s-p antibonding (conduction) band where the Fermi energy lies between the bonding and antibonding bands, and the Mn $3d$ states lie near the Fermi energy. In the hexagonal FM phase the crystalline field splits the Mn $3d$ states into three distinct energy levels labeled t_0, $t_\pm$, and e_g.[6] The t_0 orbital is directed toward the nearest-neighbor (nn) Mn along the c axis, the two $t_\pm$ orbitals are directed toward nn Mn in the basal plane, and the two e_g orbitals are directed toward nn As. It is also argued that there is a critical Mn-Mn separation ($R_c \sim 3.1$–3.7 Å) such that an itinerant description is used if the Mn-Mn separation is less than R_c and a localized description is used if the Mn-Mn separation is greater than R_c.[1,7] Since the Mn-Mn separation is less than R_c along the c axis, the t_0 and e_g levels broaden into narrow itinerant bands.[8] However, in the basal plane the $t_\pm$ levels are transitional since the Mn-Mn separation can be greater or less than R_c depending upon the crystallographic phase. Finally in their model, it is postulated that there is an intra-atomic exchange splitting between the up- and down-spin bands.

Over the entire concentration range of the solid solutions, the Mn-Mn separation distance along the c axis remains less than R_c, and thus the t_0 and e_g levels should be narrow itinerant bands. One might then expect that an itinerant-electron model may describe the pressure dependence of the FM-to-PM transition. The weak itinerant-electron theory as developed by Wohlfarth[9] and Edwards and Wohlfarth[10] has been used to study the magnetic behavior of such materials as $ZrZn_2$ [9] and the Invar alloys.[11] Recently, Wohlfarth and Bartel[12] have shown how to estimate electron-correlation effects from pressure measurements for weak itinerant FM's. In Sec. III, we extend the itinerant-electron model to include the so-called strong itinerant FM's and this model will be used to analyze the experimental data presented in Sec. II for only those solid solutions in the concentration range $x < 0.9$ where these materials exhibit a second-order behavior.

It has been established in MnAs that above a critical pressure of 4 kbars the orthorhombic phase is stabilized.[1,6] According to Goodenough and Kafalas,[6] the existence of this critical pressure is related to a critical molar volume. Within this critical molar volume there is a high- to low-spin transition which they interpret as a "drastic" change in the intra-atomic exchange energy at a maximum critical bandwidth. Then as we substitute Sb for As the lattice expands and the bandwidth decreases so that a higher critical pressure should result for stabilizing the orthorhombic phase. Since the orthorhombic phase exists in the solid solutions only over the concentration range $0.90 \leq x \leq 1$, we have measured the pertinent part of the pressure-temperature magnetic-phase diagram of the solid solution $MnAs_{0.90}Sb_{0.10}$. The maximum allowable Sb concentration was chosen to maximize the increase in critical pressure. These results will also be presented in Sec. II and discussed in Sec. III.

II. EXPERIMENTAL RESULTS

For the preparation of the solid solutions, powders of 99.9% pure Mn, As, and Sb were mixed to the desired proportions, pressed into pellets, sealed in an evacuated quartz tube, and heated to 1073 °K for 2 days. The chemically reacted product was then crushed, made into pellets, and annealed at 1073 °K for 1 day. There were no ob-