PHYSICAL REVIEW B VOLUME 47, NUMBER 9 1 MARCH 1993-I

Pressure-induced ferromagnetic states in $Sr_{14}MnAs_{11}$

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(Received 8 September 1992)

Measurements of the temperature dependence of the magnetic susceptibility of $Sr_{14}MnAs_{11}$ were made from ambient pressure to $P \leq 20$ kbars. At ambient pressure this compound is known to be a semiconductor with a Curie susceptibility down to as low as 5 K. It is found that raising the pressure to 7 kbars enhances the susceptibility somewhat and that at pressures above 10–11 kbars the susceptibility is enhanced by more than an order of magnitude and an ordered magnetic state occurs with a transition temperature that increases as the pressure is increased. This suggests that the applied pressure leads to a band-crossing transition from semiconductor to metal and a consequent exchange coupling of the Mn spins.

INTRODUCTION

Recent studies[1] of the compounds $A_{14}MnX_{11}$ (14:1:11) with A=Ca, Sr, or Ba and X=As, Sb, or Bi have shown that the 14:1:11 structure bonding can be described within the scheme of Zintl and others.[2] In particular, a formula unit consists of 14 A^{2+} cations together with the following anions; a $(MnX_4)^{9-}$ covalently bonded tetrahedron, an $(X_3)^{7-}$ chain, and 4 X^{3-} isolated anions. The representation of the structure suggests that these materials should be semiconducting. However, electrical-resistivity studies[3,4] suggest that, while the As compounds seem to be semiconductors, the compounds with either Sb or Bi are conducting at low T. Measurements of the heat capacity[5] in two of the Bi compounds also show that these compounds are metals and imply an electron density of states on the order of the d-band metals.

The magnetic properties[4,6] at ambient pressures roughly bear out the distinction noticed in the electronic properties. In $Ba_{14}MnAs_{11}$ and Sr_{14} $MnAs_{11}$, the Mn ions are well separated (about 10 Å apart for the Sr compound) and appear to be uncoupled. These compounds are simple Curie paramagnets for the temperatures studied ($T > 5$ K). Conversely, all of the metallic compounds have low-temperature magnetic states in which the Mn ions order either ferromagnetically or antiferromagnetically in a manner which is consistent with simple Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling of the local Mn spins by the conduction electrons. The $Ca_{14}MnAs_{11}$ compound complicates matters slightly in that some samples order ferromagnetically and some do not. The ferromagnetic coupling of the well-separated Mn ions in some $Ca_{14}MnAs_{11}$ samples is probably due to accidental doping of this narrow-gap ($E_g \approx 0.16$ eV) material.

The energy band gap deduced[4] from electrical-resistivity measurements on the As compounds decreases as the cation is changed from Ba to Ca suggesting that a small cation size increases the overlap of the anion wave functions resulting in a broadened valence and/or conduction band. The metallic behavior in the Sb and Bi compounds probably reflects a crossing, in these compounds, of the energy bands which make up the conduction and valence bands in the As compounds. If this is true then the insulator to metal transition is presumably driven by the large overlap of anion wave functions. One would then expect that the application of hydrostatic pressure to one of the semiconducting As compounds will increase the conduction electron density sufficiently to couple the Mn ions with the resulting appearance of an ordered magnetic state. We chose to study $Sr_{14}MnAs_{11}$ because it appears to be a simple Curie paramagnet at ambient pressure and has a smaller band gap than $Ba_{14}MnAs_{11}$.

SYNTHESIS

The details of the synthesis and structure of $Sr_{14}MnAs_{11}$ are discussed in Refs. 1 and 3. Briefly, the sample was prepared by the reaction, at 1250 °C, of the elements in stoichiometric amounts sealed with an Ar atmosphere inside a Nb tube which is itself sealed in a quartz tube. Because of the sensitivity of the elements and the reaction product to air, all of the sample preparation is done under an inert gas atmosphere. The resultant sample was analyzed both microscopically and by x-ray powder diffraction and was found to be single phase.

EXPERIMENTAL DETAILS

All measurements at ambient pressure were carried out using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The magnetization was measured in the temperature range $5 < T < 300$ K in magnetic fields less than or equal to 50 kOe. The sample was prepared by grinding polycrystalline chunks, taken from the melt, into a loose powder which was then sealed in a thin quartz tube. This sample mounting was chosen to minimize the signal from the sample holder while also minimizing contamination of the air-sensitive samples.

ac susceptibility measurements were made on a 0.245-g sample that was ground into a powder and mixed with 0.04 g of Apiezon *N* grease (to protect it from the atmosphere) before loading it into a Teflon capsule in the drybox. *N*-pentane was included in the teflon capsule as a pressure-transmitting fluid and the capsule was capped with a Teflon lid. The capsule was then removed from the drybox and loaded into the pressure cell. The pressure cell used was a standard[7] Be-Cu self-clamping device. An ac primary coil was wound around the outside of the cell and a balanced pair of pickup coils are wound on a coil form inside the primary coil near the Teflon capsule. The pressures quoted are determined from the force applied to the cell at room temperature. Thus, although the relative pressures are fairly accurate, the absolute pressure is not known to better than 1–2 kbars. The pressure cell was then bolted to a cold plate and inserted into the dewar. The ac susceptibility was measured in the temperature range $1.7 \le T \le 100$ K. Measurements were made both as the sample cooled and as the sample warmed. A typical measurement sequence consisted of balancing the coils at 100 K, monitoring the signal from the coils as the sample was cooled, balancing the coils again at 1.7 K and monitoring the signal as the sample warmed. The data do not show measureable temperature hysteresis so we will not distinguish between cooling and warming data. The data we show will include both the data taken while cooling and that taken upon subsequent warming.

The background ac pickup of the apparatus has a temperature dependence on the order of the temperature dependence of our sample both at ambient pressure and at 7 kbars. However, the background is more than an order of magnitude smaller than the sample signal for pressures above about 10 kbars. For these large signals we subtract the measured background. In addition, a small ($m = 0.01$ mg) piece of Pb was included in the pressure cell with the sample to provide an estimate of the absolute susceptibility. The volume susceptibility of the Pb was taken to be $(-4\pi)^{-1}$. The Pb signal is then subtracted from the data in order to allow fits to a Curie-Weiss susceptibility.

MAGNETIZATION AT AMBIENT PRESSURE

The inverse of the molar susceptibility of $Sr_{14}MnAs_{11}$ measured at ambient pressure and in a field of 1000 Oe is shown in Fig. 1 as a function of the temperature. Also shown is a fit to a Curie-Weiss law. The effective Bohr magneton number deduced from this fit is $4.8\pm0.1\mu_B$ and the paramagnetic Curie temperature is 0.5 ± 1 K. The Mn spins are essentially uncoupled and for temperatures above 5 K there is no sign of ordering. These data are expected upon consideration of the resistivity data[4] which showed that this compound is a semiconductor. The distance from a Mn spin to its nearest Mn neighbor is about 10 Å so direct exchange interactions are easily ruled out. Calculations[8] suggest that there is no chain of covalent bonds connecting the Mn near neighbors so one does not expect a superexchange mechanism to be significant. The magnetic dipolar coupling between Mn spins separated by 10 Å is of order 10^{-2} K. These considerations imply that the coupling between Mn spins will only be large enough for us to measure if there are conduction electrons leading to an indirect RKKY-type exchange interaction. We thus expect to find an ordered state only when the compound is metallic. A number of compounds[3,4] with the 14:1:11 structure are metallic and all of these show magnetic order at temperatures above 15 K.

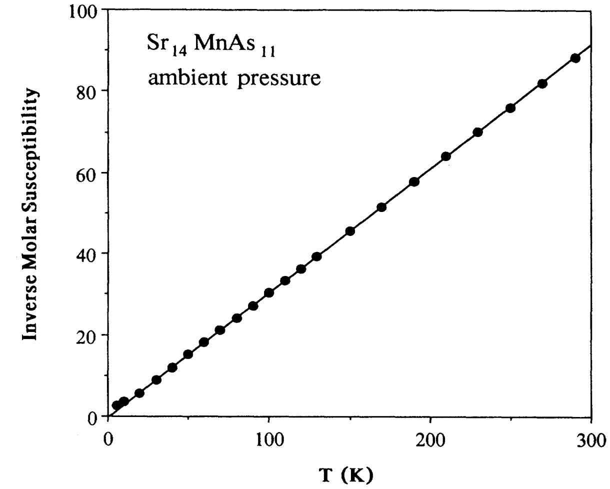

FIG. 1. Temperature dependence of the inverse molar susceptibility of $Sr_{14}MnAs_{11}$ showing simple Curie paramagnetic behavior at ambient pressure.

HIGH-PRESURE ac SUSCEPTIBILITY

The ac susceptibility was measured in the pressure cell as a function of temperature at ambient pressure and at four higher pressures 7, 11, 15, and 20 kbars. Although the 7-kbar susceptibility appeared to be larger at each temperature than that at ambient pressure, all of the data at 7 kbars were near the resolution of the apparatus so we will not consider these data in any detail. However, at pressures of 10 kbars and above the voltage pickup is much larger than background. The results for the volume susceptibility, after the normalization with the Pb signal and the subtraction of background discussed above, are shown in Fig. 2. The normalization procedure leads to an absolute value that is accurate to about 20% for the 20- and 15-kbar data. The Pb transition falls on the steep susceptibility rise for the 11-kbar data making the determination of the absolute susceptibility in this case difficult. We estimate that the absolute susceptibility at 11 kbars is accurate to about 30%. The susceptibility of the data taken above 7 kbars is enhanced by nearly two orders of magnitude over the low-pressure data suggest-

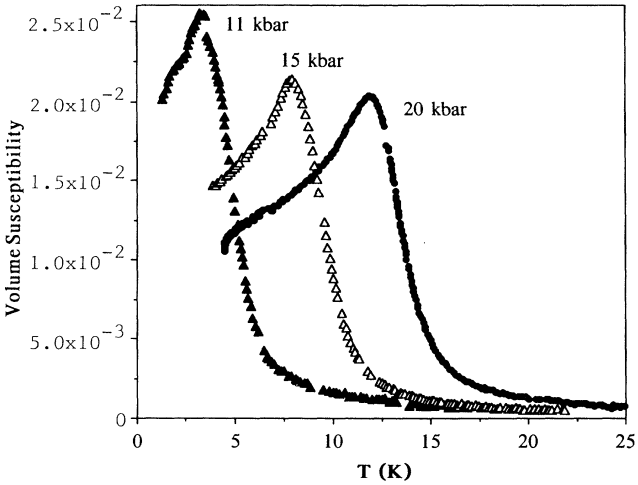

FIG. 2. Temperature dependence of the volume susceptibility of $Sr_{14}MnAs_{11}$ for three pressures above ambient pressure.

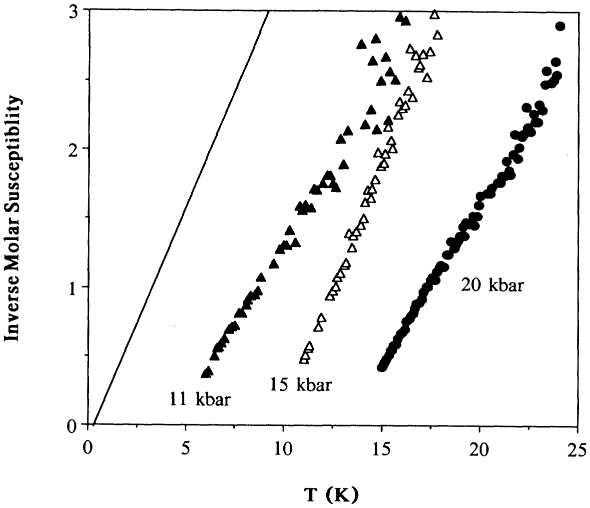

FIG. 3. Temperature dependence of the inverse molar susceptibility of $Sr_{14}MnAs_{14}$ at four different pressures. Note that the slope is independent of pressure while the temperature intercept increases as the pressure is increased.

ing that ferromagnetic correlations develop at high pressures.

For pressures of 11, 15, and 20 kbars the susceptibility develops a peak at a temperature which is quite pressure dependent. The peak susceptibility at 11 kbars appears to be higher than the peak susceptibilities at the higher pressures. The raw data also suggest that this is true but our absolute accuracy does not quite allow us to confirm this point. However, at each pressure the peak susceptibility in the data is within a factor of 2 of the demagnetization limit found earlier for a powder sample of the ferromagnet, $Sr_{14}MnBi_{11}$. This leads us to suggest that $Sr_{14}MnAs_{11}$ becomes a ferromagnet at low T under hydrostatic pressures greater than about 10 kbars. The peak one sees in the susceptibility is commonly seen in ferromagnets.[9] The temperature of the peak is sometimes identified with the transition temperature T_C. For now we just note that any reasonable definition of T_C would imply that dT_C/dP is greater than or about equal to 1 K/kbar. This value is not extraordinarily large for magnets[10] (about equal to that of Fe) but is unusual for diluted systems[11] with long-range magnetic coupling.

An examination of the susceptibility for temperatures above $1.3T_c$ suggests a simple picture of the effects of pressure. In Fig. 3 we have plotted the inverse of the molar susceptibility as a function of T for 11, 15, and 20 kbars. We have also included in the figure a line representing the Curie-Weiss fit to the SQUID data taken at ambient pressure. A linear fit to the data at each pressure gives us the Curie constant C. It appears that, within the accuracy of the experiment, the Curie constant is the same at each pressure indicating that the Mn moment does not change with pressure. However, while the paramagnetic Curie temperature (Θ) does not change much upon raising the pressure from ambient to 7 kbars, it increases by more than an order of magnitude as the pressure is increased to 11 kbars and then another factor of 2–3 as the pressure is increased to 20 kbars. Clearly, the effect of the applied pressure is to increase the exchange coupling between Mn local moments by at least two orders of magnitude.

DISCUSSION AND CONCLUSIONS

Consideration of Figs. 2 and 3 suggests that the application of hydrostatic pressure to $Sr_{14}MnAs_{11}$ dramatically increases the exchange coupling between the Mn local moments. As we discussed earlier it is likely that the resulting exchange coupling is indirect. Figure 2 is reminiscent of other dilute magnetic semiconductors. Story *et al.*[9] have shown that $Pb_{1-x-y}Sn_xMn_yTe$ changes (for small y) from a disordered magnet to a ferromagnet as the concentration of carriers is increased by changing x. These authors found a threshold in the carrier concentration below which Θ was small and did not change much with carrier density and above which Θ increased rapidly and then saturated as the carrier density was increased. They concluded that the increased magnetic coupling was due to the charge carriers via a RKKY-type interaction. Swagten *et al.*[12] explained the sharp onset concentration in terms of a two-band model. The first carriers occupy a light-hole band which yields a small exchange coupling. The sharp onset was proposed to be due to the occupation of a second band (a heavy-hole band) as the concentration was increased further. A RKKY-type coupling increases as the carrier effective mass because heavy carriers are more polarizable than light charge carriers.

We do not have a direct measurement of the carrier concentration in $Sr_{14}MnAs_{11}$ but resistivity measurements[4] at ambient pressure show an $\exp(A/T)$ dependence to the resistivity between 300 and 150 K (the lowest T for which we could measure the resistivity) with A implying an energy gap of about 0.25 eV. Thus any accidental doping has to be less than or about 10^{16} cm^{-3}. Since the accidental doping is small and should not change upon application of pressure it is likely that the change in magnetic coupling is caused by a large increase in carrier concentration. The problem is to understand the sharp onset pressure. The simplest possibility is that the application of pressure broadens the conduction and/or valence bands of the compound enough to close the band gap with the result that the high-pressure material is a metal and the exchange coupling is due to conduction electrons and holes. However, more complicated scenarios with heavy and light carrier bands may also explain these phenomena. We have begun a set of measurements of the pressure dependences of the magnetization, resistivity, and optical transmission to help us understand these materials.

ACKNOWLEDGMENTS

We thank R. N. Shelton for the use of both his SQUID magnetometer and high-pressure apparatus and P. Klavins for help with the measurements on each of these two pieces of equipment. We also thank C. Y. Fong and G. T. Zimanyi for useful discussions. This work was supported by NSF under Grants No. DMR-8913831 and No. DMR-8913855.

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