Influence of Hydrostatic Pressure on the Insulator-Metal Transition in $BaCo_{0.9}Ni_{0.1}S_{1.9}$

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High-pressure studies of $BaCo_{0.9}Ni_{0.1}S_{1.9}$, a layered transition-metal–sulfide alloy that exhibits a unique antiferromagnetic insulator to paramagnetic metal transition with decreasing temperature, are reported. Resistance measurements as a function of temperature (2–300 K) and pressure (0–0.8 GPa) are used to determine the phase diagram relating the metallic phase and several insulating phases. [S0031-9007(96)00393-6]

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The layered transition-metal–sulfide alloy system $BaCo_{1-x}Ni_xS_{2-y}$ exhibits a temperature-induced first-order insulator-metal transition for compositions in the range $0.05 \leq x \leq 0.20$ and $0.05 \leq y \leq 0.20$. This phase transition is remarkable in that it is associated with a crystalline distortion to a structure of lower symmetry that results in a transition from an antiferromagnetic insulator to a strongly correlated paramagnetic metal with *decreasing* temperature (AFI-PMM transition) [1]. Thus two common mechanisms for a metal to nonmetal transition with decreasing temperature, namely, crystalline symmetry change and antiferromagnetism, are associated with a transition that goes in the opposite direction. However, the possibility of a transition to a metallic state at low temperatures has been proposed by Phillips [2] for such ternary layered compounds containing metal-semiconductor building blocks. In this proposal the transition takes advantage of the lowering of energy by improved screening of long-range ionic potentials. Clearly much experimental work is needed to elucidate the nature of this AFI-PMM transition before a detailed mechanism can be invoked to account for this unusual transition. The influence of pressure on the AFI-PMM transition temperature is important information for identifying the correct mechanism.

Above the temperature of the AFI-PMM transition, these alloys are isostructural with $BaNiS_2$ which has a tetragonal structure [3] consisting of Ni-S sheets separately by slightly distorted rock salt Ba-S layers. Based on the band structure calculation [4] for $BaNiS_2$, one would expect the entire $BaCo_{1-x}Ni_xS_{2-y}$ series to be metallic as the result of partially filled σ^* bands near the Fermi energy. However, for the range of x where the sulfur deficient alloys undergo the AFI-PMM transition, all compounds exhibit thermally activated semiconducting behavior in the resistivity and local moment behavior in the magnetic susceptibility at temperatures above T_N similar to that seen in $BaCoS_2$. Thus it appears that the alloys are semiconducting in the high-temperature paramagnetic (PMI) phase as the result of strong electron correlations; i.e., they are Mott-Hubbard insulators. As the temperature is lowered there is a second-order magnetic PMI-AFI phase transitions. That this is a transition to a phase with long-range antiferromagnetic order has been confirmed by neutron diffraction on powered samples [5]. As the temperature is further reduced there is a first-order AFI-PMM transition with large hysteresis between heating and cooling. Single crystal x-ray diffraction studies have shown that there is a lattice distortion to lower symmetry structures [6]. In the low-temperature phase the resistivity and magnetic susceptibility are nearly temperature independent, characteristic of a paramagnetic metal. Preliminary results on the structural, electrical, and magnetic properties of these alloys as a function of composition have been published [1]. Further studies of these properties have been completed and the extensive results will be published elsewhere.

In this Letter we report on the influence of pressure on the AFI-PMM transition in a $BaCo_{0.9}Ni_{0.1}S_{1.9}$ sample. Resistance measurements as a function of pressure and temperature were performed. These measurements included cycles of cooling and warming at constant pressures and also of applying and releasing the pressure at constant temperatures. The results of these measurements are used to determine the temperature-pressure phase diagram. The AFI-PMM phase boundary curve is exceptional in that the application of pressure suppresses the temperature of the transition to the metallic phase.

The sintered polycrystalline sample of the single-phase $BaCo_{0.9}Ni_{0.1}S_{1.9}$ studied was prepared by conventional solid-state reaction techniques. Equal numbers of moles of BaS, NiS, and $CoS_{0.86}$ were mixed, pressed into a pellet, and sealed in quartz tubing at a pressure less than 10^{-5} torr. The sample was heated to 300 °C at 5 °C/min and held for 4 h, then raised to 910 °C at 10 °C/min and held there for 12 h. The sample was cooled, ground, pressed, and resealed. Then it was heated again to 910 °C, held for 72 h, and quenched to room temperature by rapid removal from the furnace. The quenching is required

to avoid producing a Ba_2CoS_3 contaminant phase [7]. Finally, the sample was annealed by heating to 550 °C. Alloys that are rapidly quenched from high temperatures do not exhibit the AFI-PMM transition if they are not annealed at the lower temperature [8].

For the resistance measurements a bar was cut from the pellet and copper wire contacts attached with silver epoxy. The electrical resistance was determined using a standard four-wire configuration; the excitation current was reversed during each measurement to eliminate thermal voltage. Currents ranging from 1 mA down to 10 μA were used. The lower currents were required to prevent sample heating due to increasing contact and sample resistance with repeated temperature and pressure cycling through the transition. Pressure was generated by a helium gas compressor system from Harwood Engineering and measured with a calibrated manganin coil maintained at room temperature. A sizable "dead volume" at room temperature reduces the decrease of pressure upon cooling to 30 K to less than $\sim$10%. The CuBe pressure cell is suspended in a continuous flow cryostat from a CuBe capillary connected to the compressor. Temperature was measured with two sets of calibrated platinum ($T > 20$ K) and carbon ($T < 20$ K) resistors mounted at either end of the pressure cell. Details of the high pressure technique can be found elsewhere [9].

At room temperature (RT), which is above $T_N \simeq 280$ K, measurements of resistance versus pressure showed a reversible decrease of resistance with increasing pressure. The pressure coefficient of resistivity, $\partial \ln\rho/\partial P$, was independent of pressure over the entire range of pressures applied (0.0 to 0.6 GPa). Thus the RT behavior is typical of a semiconductor with a excitation gap that decreases linearly with pressure. For the coefficient we obtained $\partial \ln\rho/\partial P \approx -3.1\ \mathrm{GPa}^{-1}$ and thus $kT\partial \ln\rho/\partial P \approx -80$ meV/GPa for the RT shift in the electrical activation energy. At zero applied pressure the activation energy of this sample, determined from the temperature dependence of the resistance, is approximately 60 meV. Hence at slightly higher pressures than were available one would expect a continuous transition to metallic behavior, but this is unrelated to the PMM phase that occurs at zero applied pressure at lower temperatures.

The resistance as a function of temperature was measured for fixed pressures between 0 and 0.6 GPa. The pressure was applied at RT, and the resistance was measured as the sample was cooled to 5 K and warmed back to RT. Figure 1 shows the measured resistance versus temperature for one series of measurements at increasing pressure intervals of approximately 0.1 GPa. Here only the cooling curves are displayed for clarity. Figure 2 shows both the cooling and warming curves for two of these measurements near 0.2 and 0.5 GPa. In the cooling curves of Fig. 1, the sharp AFI-PMM transition is observed only for $P < 0.3$ GPa [10]. The temperature

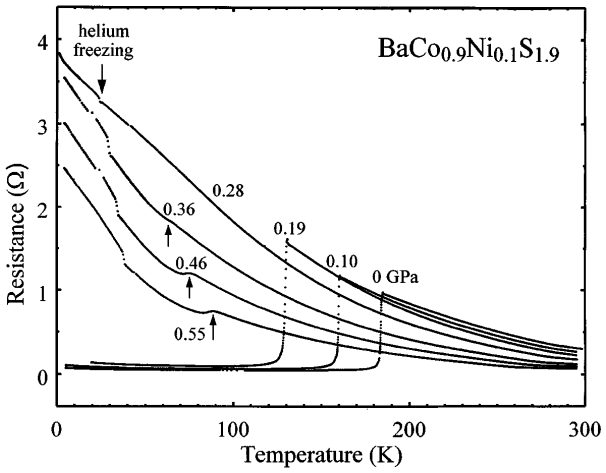

FIG. 1. The resistance of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ as a function of temperature on cooling for increasing pressures between 0 and 0.6 GPa.

of this AFI-PMM transition rapidly *decreases* with pressure. For $P > 0.3$ GPa there is another first-order transition that causes a small change in resistance. In this case, where the sample remains semiconducting, the transition temperature *increases* with pressure. Presumably this transition involves a change in crystal structure, and one would also guess that the low-temperature insulating phase is magnetically ordered. However, since we have not investigated the properties of this phase, we simply denote this transition by AFI-I′. The anomalies seen in the curves in Figs. 1 and 2 in the temperature range 20–40 K for $P \geq 0.3$ GPa are associated with the freezing of the helium pressure medium. In Fig. 2 one sees the large thermal hystereis associated with both types of transitions. In both cases this hysteresis increases with decreasing transition temperature. The increase in resistance after cooling and warming through the transitions is probably due to strain-induced defect scattering in this sintered polycrystalline sample.

The antiferromagnetic transition can also be identified by careful inspection of the resistance versus temperature curves above 250 K. The logarithmic derivative of the resistance has a local maximum at T_N. The insert in Fig. 2 shows this peak in the logarithmic derivative. This method of estimating T_N has been shown to be consistent with values derived from magnetic susceptibility data for these materials [1]. T_N decreases from 280 to 255 K with applied pressure increasing from 0 to 0.6 GPa.

To investigate the AFI-PMM transition by isothermal measurements, we cool the sample at zero applied pressure to a temperature below the transition. Pressure is then applied to the metallic sample at fixed temperature. At sufficiently high pressure there is a transition to an insulating phase. The pressure is then released in order to observe the transition back to the metallic phase. Figure 3

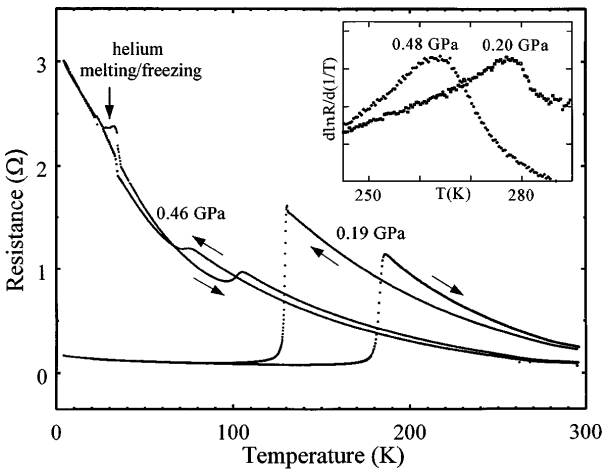

FIG. 2. The resistance of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ as a function of temperature at pressures of 0.2 and 0.5 GPa for cooling followed by warming. The inset shows the peak in the logarithmic derivative of the resistance used to determine the Néel temperature.

shows the measured resistance as a function of pressure at 77 K for applying and then releasing the pressure. The results for several measurements at $T > 100$ K clearly show the transition temperature decreasing with pressure while measurements at $T < 70$ K show the temperature increasing. This difference reflects the two distinct insulating phases seen in the isobaric measurements. The very large hysteresis in pressure of the insulator-metal transition increases as the temperature at which the pressure is cycled is decreased. For $T \leq 40$ K, the transition from the metallic to the insulating phase with increasing pressure could not be investigated owing to the freezing of the helium pressure medium. To observe the insulator to metal transition for $T \leq 40$ K, the sample was made insulating by applying pressure at 80 K before cooling to the desired temperature for releasing the pressure. This resulted in a transition from the low-temperature insulating phase to the metallic phase.

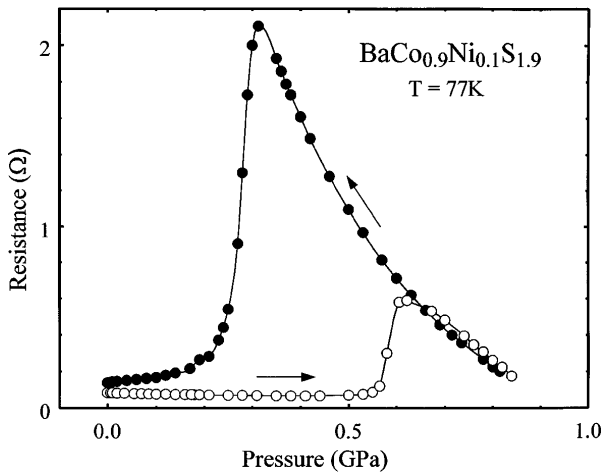

FIG. 3. The resistance of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ at 77 K as a function of pressure, first applied and then released.

A summary of all of our results for transition temperatures as a function of pressure is presented in Fig. 4. This figure is also an overview of the phase diagram for $BaCo_{0.9}Ni_{0.1}S_{1.9}$ that is derived from the measurements. The measured transition temperatures are plotted with symbols that identify the type of transition and the directional path used to make the transition. For the first-order transitions the phase boundaries are made uncertain by the hysteresis. The solid lines are crude estimates for the actual equilibrium coexistence curves for the different phases. The AFI-PMM curve is a straight-line fit by the averages of the transition temperatures for cooling and warming at the different pressures. We use the constant pressure results since these transitions are much sharper than those at constant temperature. Note that the averages of the transition pressures for applying and releasing the pressure are consistent with this line for $T \geq 100$ K. The AFI-I′ curve is also a straight-line fit by the averages of the transition temperatures for cooling and warming. Although there is no theoretical justification for assuming the two phases are in equilibrium at the midpoint of the thermal hysteresis, it is expected to give a reasonable estimate

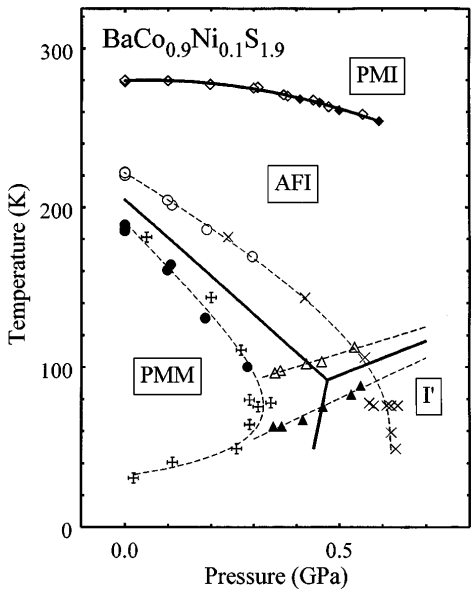

FIG. 4. Transition temperatures and pressures and derived T-P phase diagram of $BaCo_{0.9}Ni_{0.1}S_{1.9}$. Transition temperatures at constant pressures are denoted by circles (●, ○), triangles (▲, △), and diamonds (◆, ◇) for the AFI-PMM, AFI-I′, and PMI-AFI transitions, respectively; solid and open symbols for cooling and warming, respectively. Transition pressures at constant temperatures for entering and exiting the PMM phase are denoted by crosses (+) and x's (×). Solid lines are the estimated phase boundaries. The different phases are paramagnetic insulator (PMI), antiferromagnetic insulator (AFI), paramagnetic metal (PMM), and uncharacterized insulator (I′).

for the coexistence curve. The PMI-I′ coexistence curve is the most difficult to estimate since transitions were observed only in the constant temperature data and only for decreasing pressure at the lower temperatures. The straight line drawn was constrained to join the other two curves at their intersection and fit the averages of the transition pressures. There is no basis for extrapolating this straight line to temperatures below 40 K.

For the AFI-PMM, AFI-I′, and PMM-I′ coexistence curves drawn $dT/dP \simeq -240$, 105, and 1300 K/GPa, respectively. The first two values should be rather good estimates, but the last value only an order of magnitude estimate. At zero applied pressure the volume change $\Delta V_{\mathrm{AFI}\to\mathrm{PMM}} = 0.6 \pm 0.2$ cm^3/mole has been determined by single-crystal x-ray diffraction measurements [11]. Hence, from the Clausius-Clapeyron equation, $\Delta S = \Delta V/(dT/dP)$, the entropy change $\Delta S_{\mathrm{AFI}\to\mathrm{PMM}} = -0.6 \pm 0.2$ cal/K mole. We do not have measured volume changes with which to calculate the other entropy changes. However, $\Delta S_{\mathrm{PMM}\to\mathrm{I}'}$ should be much smaller in magnitude than $\Delta S_{\mathrm{AFI}\to\mathrm{PMM}}$ owing to the large value of dT/dP. Thus $\Delta S_{\mathrm{I}'\to\mathrm{AFI}} \approx 0.6 \pm 0.2$ cal/K mole from the conservation of entropy around the triple point and the assumption that ΔS is essentially constant where dT/dP is constant. In that case $\Delta V_{\mathrm{I}'\to\mathrm{AFI}} \approx 0.4\Delta V_{\mathrm{AFI}\to\mathrm{PMM}}$ and $\Delta V_{\mathrm{I}'\to\mathrm{PMM}} \approx 1.4\Delta V_{\mathrm{AFI}\to\mathrm{PMM}}$.

In summary, we have characterized the temperature-pressure phase diagram for $BaCo_{0.9}Ni_{0.1}S_{1.9}$ for temperatures between 40 and 300 K and pressures between 0 and 0.6 GPa. For temperatures above the AFI-PMM phase boundary the influence of pressure on this semiconducting material is quite ordinary. However, the AFI-PMM transition is quite remarkable. First, there is the exceptional requirement that the insulating phase have a larger entropy than the metallic phase despite the fact that it is magnetically ordered. Second, there is the exceptional coexistence curve that shows a rapid decrease with increasing pressure for the temperature of the insulator to metal transition. A possible explanation for the extra entropy in the AFI phase is that the sulfurs in the $Co_{1-x}Ni_xS$ layers are in double wells. There is some experimental indication for this in $BaCoS_2$ [12]. In addition to identifying the source of the additional entropy, one needs to understand why the structure should distort in such a manner as to make the materials metallic when the temperature is decreased. Note that at higher pressures we have the usual situation of a low-temperature insulating phase with the AFI-I′ transition. A possible explanation, based on ideas of Phillips [2], is that this sulfur deficient layered structure can be expected to have strong internal electric fields. The energy would therefore be significantly lowered by improved screening. As the number of carriers in the semiconducting phase decreases with decreasing temperature, the electric field energy can become so large that it is favorable to have a structural distortion to a metallic phase. Since pressure increases the number of carriers at a given temperature in the semiconducting phase by decreasing the excitation gap, pressure should lower the transition temperature, as observed.

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[6] X-ray diffraction measurements as a function of temperature were performed on several small single crystals. For each one of the crystals measured, we found that the single crystal did not transform into the same crystal structure each time it was lowered through the transition temperature. The several different monoclinic structures observed have different unit cells, but otherwise are closely related, and were common to all the crystals. These unit cells have dimensions perpendicular to the $Co_{0.9}Ni_{0.1}S$ layers that are various approximate multiples of the corresponding dimension in the unit cell of the tetragonal insulating phase.
[7] Ba_2CoS_3 is a quasi-one-dimensional antiferromagnet that exhibits a broad maximum in the magnetic susceptibility near 125 K. Quantities of this contaminant much too small to be detected by x-ray diffraction are easily seen in magnetic susceptibility measurements. Susceptibility measurements of our sample showed it to be free of this contaminant phase.
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[10] Although the AFI-PMM transition was not observed at 0.28 GPa in the measurement series of Fig. 1, it was observed at this pressure at 100 K when the sample was rapidly cooled (>10 K/min) from 120 to 77 K in an earlier run.
[11] The large uncertainty in our estimate of the volume change at the transition is due to variations in the volume per mole for the different unit cells that were seen in the metallic phase.
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