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The transport properties in strongly correlated $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$

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Abstract

Layered tetragonal $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_2$ contains high-spin Co(II) in octahedral sites and is an insulator. Hole doping by introducing sulfur vacancies results in a polaronic conductivity and produces a transition to a monoclinic metallic phase with a nearly isotropic conductivity. Pressure $P > 1.5$ kbar suppresses the monoclinic phase and at $P > 10$ kbar the high temperature tetragonal phase is transferred to an isostructural metallic phase containing low-spin Co(II). The single-crystal resistivity along the c -axis and in the a - b plane of high-pressure, tetragonal $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ is shown to be highly anisotropic and to resemble that of the overdoped superconductive system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

1. Introduction

A theoretical description of the electronic behaviour of strongly correlated systems on the approach to and on crossover of the transition from itinerant to localized electronic behaviour is one of the more challenging problems in condensed-matter physics. For example, no consensus has been reached on a description of the electronic behaviour of the superconductive cuprates after 15 years of extensive and intensive study. Superconductivity in the cuprates occurs in a narrow doping range between a Mott insulator and a metallic phase. The transport properties of these and other highly anisotropic, strongly correlated systems are not described by conventional theory [1]. In the cuprates, metallic-like conduction is formed at room temperature with only 0.01 hole/Cu in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. An understanding of the effect of doping on these Mott insulators appears to be a key that could unlock this problem.

Like the parent compound of the high- T_c cuprates, tetragonal (HTT) BaCoS_2 is a layered Mott insulator near a cross-over to itinerant-electron behaviour; $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ undergoes a single-valent insulator–metal (IM) transition on substitution of $x = 0.25$ Ni(II) for Co(II) [2]. The HTT insulator phase contains high-spin Co(II). In order to explore the effect of hole doping on the Mott-insulator phase near crossover, sulfur vacancies were introduced into the Mott insulator $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ [3]. In this material, unlike in the cuprates, a large concentration of holes fails to produce a metallic conductivity in the HTT phase at ambient pressure, but doping does introduce a low-temperature, monoclinic (LTM) phase that is metallic. In this paper, we report the pressure dependence of single-crystal resistivity for $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$. A recent structural refinement of the LTM phase [4] shows it has a larger volume than the HTT phase,

and we report that the LTM phase is suppressed by a hydrostatic pressure $P > 1.5$ kbar. The structural refinement also showed that the Co(II) are displaced from octahedral sites in the HTT phase to tetrahedral sites in the LTM phase, which allows interpretation of a nearly isotropic metallic resistivity. However, pressure $P > 10$ kbar stabilizes a tetragonal metallic phase that is highly anisotropic in accordance with a transition to octahedral-site low-spin Co(II) in this layered structure. Comparison of the resistivity data for the high-pressure tetragonal phase with those for overdoped compositions in the superconductive $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system shows striking similarities that invite exploration of this phase at lower hole doping. Similar studies have previously been done on $\text{NiS}_{2-x}\text{Se}_x$, LnNiO_3 and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$. However, the first two single-valent systems have structures that support isotropic three-dimensional conductivity and the last one becomes metallic only at a hole concentration that is much higher than that in the optimally doped cuprates.

2. Experimental details

Single crystals of $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ were grown by vapour transport from a starting charge of $\text{BaCo}_{0.92}\text{Ni}_{0.08}\text{S}_2$. About 2 g pellet of the charge material was placed at one end of a 5 cm long quartz tube that was then sealed under a vacuum of 10^{-3} Torr. The sealed tube was loaded into a tube furnace with the pellet located at the centre of the hot zone. The sealed tube was heated at a rate of 250°C h^{-1} to 1050°C , held at this temperature for about 2 h before cooling at 2°C h^{-1} to 950°C and finally quenched in water. Black, platelike crystals as large as $5\text{ mm} \times 5\text{ mm} \times 0.1\text{ mm}$ formed at the cooler end of the tube. A $1.0\text{ mm} \times 0.5\text{ mm} \times 0.05\text{ mm}$ crystal portion having a mirror-like surface was chosen for measurement of transport properties under pressure and thermal conductivity. The Ni concentration $x \approx 0.1$ in the crystal was determined from the Néel temperature T_N in accordance with the plot of T_N versus x established [6] for $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$. The as-grown crystals were insulators and showed no transition to the LTM phase down to lowest temperatures. In order to introduce sulfur vacancies, the crystals were sealed in a quartz tube under 10^{-3} Torr together with a polycrystalline sample of $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ and heated to 920°C followed by an anneal at 500°C for 6 h. The resulting sulfur deficiency of a crystal was taken to be the same, $y = 0.13$, as that of the polycrystalline material with which it was equilibrated. The sulfur deficiency of the polycrystalline material was determined by a standard atomic-emission spectrum.

A four-probe method was used to measure the resistivity under pressure. Cu wires (0.0005" diameter) were attached to the crystals with silver epoxy. The measurements under pressure were carried out in a self-clamped Be–Cu cell using silicone oil as the pressure medium. The brittle crystals shattered into small pieces after one or two thermal cycles through T_t . However, the crystals retained their shape over many thermal cycles if kept under a pressure of several tens of atmospheres. The original $\rho(T)$ is reproducible after the pressure is released from a high value to a lower one greater than ambient.

3. Results and discussion

The temperature dependences of the resistivity along the c axis and within the a – b plane under pressure are plotted in figures 1 and 2. A few important features are highlighted here:

- (a) the transition at T_{t1} to the LTM phase is suppressed at pressures $P > 1.5$ kbar as found in the previous study on ceramic samples;
- (b) an insulator-to-metal transition occurs within the tetragonal phase under pressures $P > 10$ kbar.

Most importantly, our measurements on single-crystal samples characterize precisely the LTM, the HTT-insulator and HTT-metallic phases. The pressure dependence of the transition

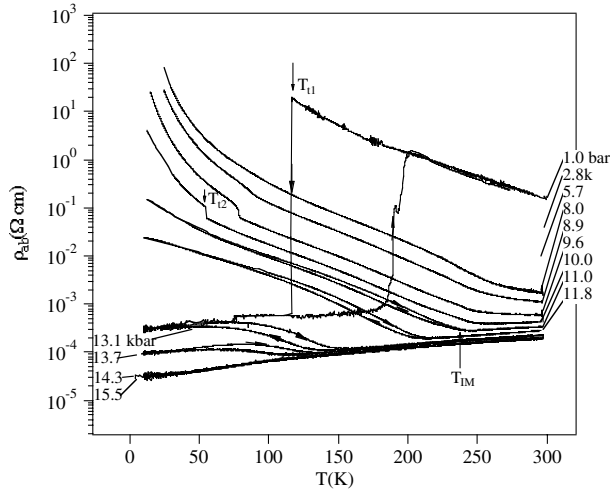


Figure 1. The temperature dependence of the resistivity within the a - b plane of single-crystal $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ under pressure.

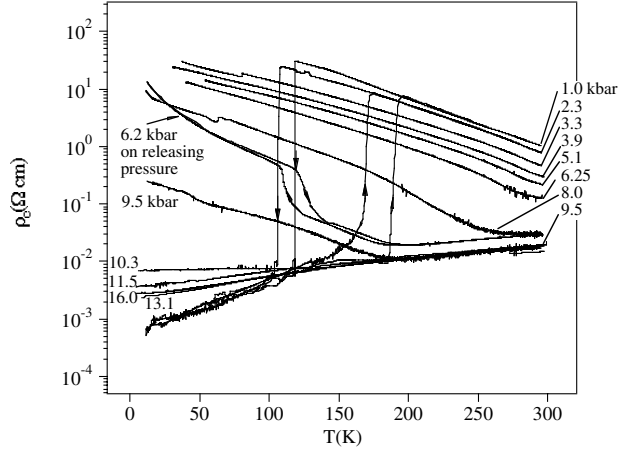


Figure 2. The same as figure 1 along the c axis.

temperatures between these phases is summarized in the phase diagram of figure 3(a) along with the pressure dependences of the resistivity at 290 and 50 K, which are plotted in figure 3(b). Three phase boundaries are encountered on increasing pressure at $T = 50$ K whereas one phase boundary is crossed at $T = 290$ K.

In contrast with the high- T_c cuprates, layered $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ with a nominal hole concentration $x = 0.26$ remains an insulator and shows little anisotropy of ρ_c versus ρ_{ab} . The lack of two-dimensional character is correlated with the high-spin state of Co(II) [7] where the Fermi energy is located in a band of t_2 orbital parentage. However, the metallic phase under pressures $P > 10$ kbar shows a highly anisotropic conductivity. The observation of a crossover from three- to two-dimensional conductivity in the HTT phase at T_{IM} allows us to associate the insulator-to-metal transition with a change from high-spin Co(II) to low-spin Co(II); in the low-spin state, the Fermi energy falls inside the $\sigma_{x^2-y^2}^*$ band as shown in the schematic diagram of figure 4. It is with the low-spin state of layered $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ that a comparison

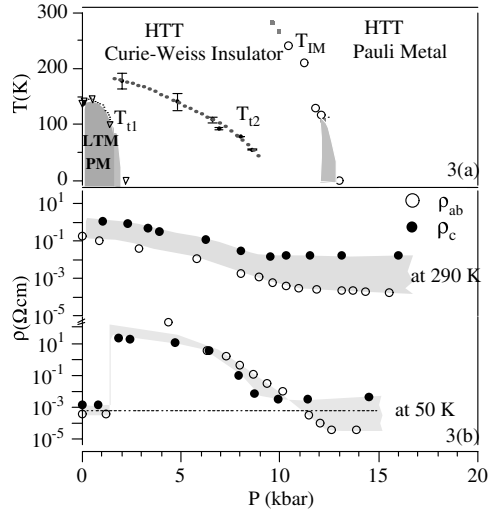


Figure 3. (a) The phase diagram of and (b) the pressure dependence of the resistivity at 290 and 50 K.

to the high- T_c cuprates should be made. Figures 5 and 6 show the temperature dependence of ρ_{ab} and ρ_c in the metallic HTT phase together with the corresponding curves of slightly overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The power law $\rho \sim T^{1.4}$ is held over a wide temperature range for both ρ_{ab} and ρ_c as shown in the insets of figures 5 and 6. The well known characteristics of the transport properties of the high- T_c cuprates include the following:

- (a) the conductivity in the basal plane falls into the ‘bad metal’ range, i.e. $10^4 \Omega^{-1} \text{cm}^{-1}$;
- (b) two-dimensional conductivity;
- (c) linear temperature dependence of the resistivity in the range from T_c to several hundreds of Kelvin in the phases near optimal doping;
- (d) a crossover from $\rho \sim T$ to $\rho \sim T^{1.5}$ with increasing hole density from the optimal doping to overdoping [8]; and
- (e) a crossover from semiconductive conductivity to metallic conductivity along the c axis occurs at optimal doping [9].

The temperature dependence of the resistivity of metallic low-spin $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ shown in figures 5 and 6 matches (a), (b), (d) and (e) if $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ is compared with the overdoped cuprate. These features of the transport properties cannot be rationalized within Boltzmann’s model [1] and point to a new mechanism of electron–electron, electron–lattice interaction in two dimensions, strongly correlated systems. The matching in almost all aspects between the overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ makes it extremely interesting to study the transport properties of the low-spin, optimally doped $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{2-y}$ stabilized under pressure. Among the transition-metal oxides, only the copper oxides show both unique transport properties and superconductivity below T_c . The crossover from localized to itinerant electronic behaviour, which appears to be an important factor behind the unusual physical properties, has been seen in several narrow-band systems. The manganese oxide perovskites operating on a high-spin Mn(IV)/Mn(III) redox couple are distinguished by a coupling of the spins of the conductive electrons of e-orbital parentage to localized $S = 3/2$ spins of a half-filled t_2^3 manifold; they exhibit the colossal magnetoresistance (CMR) phenomenon. The sulfides are to be distinguished from the oxides by $\text{S}^{2-}:3p^6$ bands that are higher in energy than the $\text{O}^{2-}:2p^6$ bands. As a result, the transition-metal redox energies are at the top of the $\text{S}^{2-}:3p^6$ bands at a lower formal valence; they are at the top of the $\text{O}^{2-}:2p^6$ bands at a

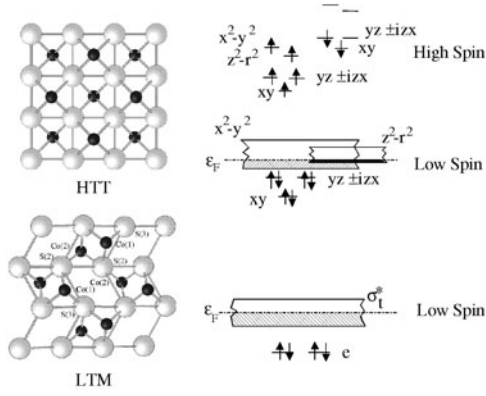


Figure 4. Crystallographic structure of the HTT phase and LTM phase (after [4]) together with the schematic energy diagram.

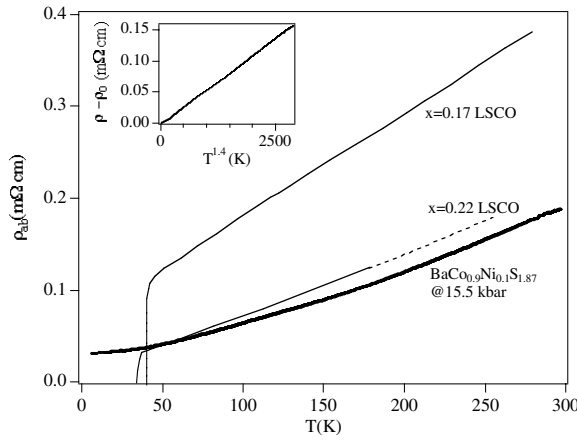


Figure 5. The temperature dependence of the resistivity within the basal plane for the HTT metallic phase of $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (after [9]). Inset: ρ_{ab} versus T plotted in the power law for $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$.

higher formal valence. Where the cation redox energies in an ionic model drop below the anion p^6 energies, the antibonding d-like redox energies become pinned at the top of the anion p^6 bands, but the ratio of anion-p to cation-d admixture in the formal redox couple increases dramatically. That is why low-spin octahedral-site Co(II) and Ni(II) are encountered in sulfides whereas these valence states represent a localized, high-spin configuration in oxides. Moreover, low-spin octahedral-site Co(II): $t_2^6\sigma_{x^2-y^2}^*d_{z^2}^0$ in layered sulfides is comparable to the Cu (II): $t_2^6d_{z^2}^2\sigma^*d_{x^2-y^2}$ in the layered cuprates; in each case a half-filled σ -bonding $x^2 - y^2$ band coexists with a filled t_2^6 configuration and either empty or filled z^2 orbitals. The low-spin Ni(II) has one additional electron that presumably occupies an overlapping σ^* band, which makes it difficult to know how to think about the doping of the σ^* band in $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$. It would be particularly instructive to investigate stabilization under high pressure of a sulfur-stoichiometric low-spin Co(II) BaCoS_2 . If it should prove to be a Mott insulator, the analogy with La_2CuO_4 would be striking.

A transition to a metallic phase at low temperature like that found in $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ is unusual. In the mixed-valent CMR manganites, the change from polaronic to metallic conductivity with decreasing temperature is associated with the onset of long-range ferromagnetic order below a Curie temperature T_c . Figure 3 shows that the LTM metallic phase has a nearly isotropic conductivity; the average of ρ_{ab} and ρ_c is about the same as that in the highly anisotropic, low-spin HTT phase. The isotropic conductivity is consistent with the observation [4] of a displacement of the high-spin Co(II) from octahedral sites to the

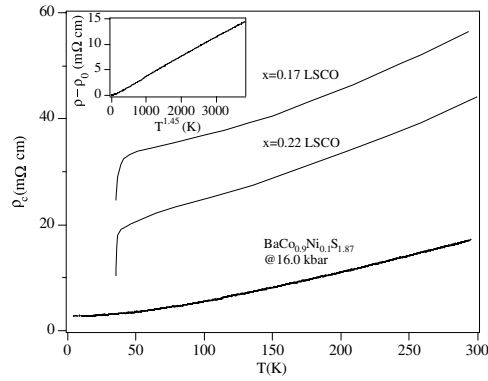


Figure 6. The same as figure 5 along the c axis.

tetrahedral sites as low-spin Co(II): $e^4 \sigma_t^{*3-z}$ with a less than half-filled σ_t^* band of t_2 -orbital parentage. Tetrahedral sulfur coordination increases the volume somewhat even though the Co(II) is transferred from the high-spin to the low-spin state, which is why the LTM phase is suppressed by hydrostatic pressure relative to the high-spin Co(II) HTT phase.

4. Conclusion

Three distinguishable phases have been identified in single-crystal measurements of the resistivities ρ_c and ρ_{ab} of layered $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.87}$ under different hydrostatic pressures. A metallic, monoclinic LTM phase below $T_{t1} = 150$ K at ambient pressure is suppressed by $P > 1.5$ kbar; it has low-spin Co(II) in tetrahedral sites and a nearly isotropic conductivity. A polaronic HTT phase with octahedral-site high-spin Co(II) transforms under pressure $P > 10$ kbar to an isostructural phase with low-spin Co(II); the low-spin-Co(II) HTT phase has a highly anisotropic resistivity ratio $\rho_c/\rho_{ab} \gg 1$ and a metallic conductivity with several characteristics similar to those of slightly overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. These electronic features can be reconciled with less than half-filled σ_t^* and $\sigma_{x^2-y^2}^*$ bands, respectively, for the LTM and low-spin HTT phases. The data suggest that an investigation of sulfur-stoichiometric BaCoS_2 under high pressure would be instructive. If the low-spin-Co(II) HTT phase can be stabilized and it proves to be a Mott insulator, the analogy with La_2CuO_4 would be compelling.

Acknowledgments

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