Magnetic properties and specific-heat studies of the metal-insulator transition in BaCo$_{0.9}$Ni$_{0.1}$S$_{2-y}$

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We have investigated the BaCo$_{0.9}$Ni$_{0.1}$S$_{2-y}$ system which crystallizes in the tetragonal BaNiS$_2$-type structure, by several complementary experimental techniques. The insulating stoichiometric compound ($y=0$) is antiferromagnetically ordered $T_N=265$ K. The sulfur-deficient compounds undergo a first-order metal-insulator (MI) transition at $T_s=220$ K. Mössbauer studies on ^{57}Fe-doped materials show that the magnetic structure observed in the insulting state persists in the metallic state without any discontinuity in the magnetic properties. In addition, this MI transition is accompanied by (i) a slight distortion in the tetragonal BaNiS$_2$ structure, and by (ii) a valence transition of divalent Ni^{2+} ions to monovalent Ni. Specific-heat measurements show an anomaly at the MI transition, and the entropy associated with this transition is 1.6 (J/mol K) and is associated with both crystallographic and valence transitions.

INTRODUCTION

The BaCo$_{1-x}$Ni$_x$S$_{2-v}$ compounds are excellent materials for systematic experimental studies that can lead to a better understanding of magnetic and electronic properties of solids that are of theoretical and practical importance. Compared to the stoichiometric ternary BaMS$_2$ compounds (where M =Co or Ni), the two extra degrees of freedom, namely, the presence of two transition elements and the deficiency of sulfur, considerably increases not only the number of available compounds, and correspondingly a large variety of crystal structure types, but also allows much more flexibility by changing each of the two variables separately, in modifing their magnetic and electronic properties. Special interest is concentrated on nickel because of its mixed valence state.

Several interesting physical properties of BaNiS$_2$ have recently been reported.[1,2] This compound crystallizes in the tetragonal system, space group $P4/nmm$, with two formula units in each unit cell. The basic structural unit consists of a nickel atom which is coordinated to five sulfur atoms at the corners of an almost regular square pyramid. The Ni$_2$S$_2$ sheets determine the physical properties of this compound much as do the CuO$_2$ planes in the high-T_c superconductor YBa$_2$Cu$_3$O$_7$. In contrast to the pyramids of the Cu(2)-O planes in YBa$_2$Cu$_3$O$_7$, here, the apical sulfurs of the edge-sharing pyramids alternate above and below the plane formed by the bases of the pyramids. The electrical resisitivity of BaNiS$_2$ is metallic in nature and the nearly temperature-independent susceptibility is due to a contribution of conduction electrons, i.e., BaNiS$_2$ exhibits Pauli paramagnetism. BaCoS$_2$ crystallizes in an orthorhombic structure, which is a monoclinic distortion of the tetragonal BaNiS$_2$ structure. The cobalt is also five coordinated, forming nearly square CoS$_5$ pyramids, and only the local symmetry of the atoms

is reduced to twofold orthorhombic. In contrast to BaNiS$_2$, BaCoS$_2$ is a semiconductor (Mott insulator), and magnetic studies indicate that the compound is antiferromagnetically (AFM) ordered at $T_N=300$ K.[3]

The mixed BaCo$_{1-x}$Ni$_x$S$_{2-y}$ system crystallizes in the BaNiS$_2$-type structure even for $x=0.1$,[2] and the electrical and magnetic properties depend strongly on the Ni and S concentrations. The salient physical features are that (1) the substitution of Ni for Co decreases the a lattice constant, while the c lattice constant remains unchanged but no evidence for such changes are produced by sulfur vacancies. (2) A first-order phase metal-insulator (MI) transition (at T_s) from insulating semiconducting (like BaCoS$_2$) to metallic behavior (like BaNiS$_2$) for $0.05 < y < 0.2$ occurs at high temperatures. (3) T_s depends strongly on y and is shifted from about 150 K for $y=0.05$ to 220 K for $y=0.2$. (4) In BaCo$_{1-x}$Ni$_x$S$_{2-y}$ (for $y=0$) the antiferromagnetic transition at $T_N=300$ K found in BaCoS$_2$, decreases dramatically with increasing Ni concentration and disappears for $x>0.25$. This decrease is faster than might be expected from simple magnetic dilution resulting from the substitution of nonmagnetic Ni for Co.[4] On the other hand, for a given x, the decrease of sulfur content increases T_N slightly. (5) Below T_s (in the metallic state), the susceptibility for BaCo$_{1-x}$Ni$_x$Si$_{2-y}$ is approximately temperature independent. The intriguing question, whether the magnetic order which exists at high temperatures (when the system is semiconducting) persists even in the metallic region, is the main subject of this paper.

In recent papers[5,6] we have used the Mössbauer spectroscopy (MS) studies on dilute Fe doped in the high-T_c materials and have shown that Fe is a reliable probe of the magnetic behavior of the Cu site. We have adapted this method to study the magnetic behavior of BaCo$_{0.9}$Ni$_{0.1}$S$_{2-y}$. Based on MS and several complemen-

tary experimental techniques, we show that, indeed, the magnetic order observed clearly at high temperatures persists in the metallic state without any discontinuity. In addition, x-ray-diffraction analysis indicates that the electrical first-order phase transition is accompanied by a slight distortion in the tetragonal structure. Specific-heat measurements show an anomaly at the MI transition and the entropy associated with this transition is 1.6 (J/mol K). A second sharp anomaly in the C_p curve above T_s is observed but its nature is not yet known.

EXPERIMENTAL DETAILS

Ceramic samples with nominal composition $BaCo_{1-x}Ni_xS_{2-y}$ and the ^{57}Fe-doped material [~0.5% substituted for the whole Co(Ni) content] were prepared by solid-state reaction. Prescribed amounts of BaS, Ni, Co, S, and ^{57}Fe were mixed and pressed into pellets, sealed in quartz tubing at a pressure of 8×10^{-5} torr and preheated to 300°C for about 24 h. The products were cooled, reground, sealed again and reheated at 940°C for 3 days. To avoid formation of the Ba_2CoO_3 phase at 900°C the quartz tubes were quenched to room temperature in cooled water. Powder x-ray-diffraction (XRD) measurements were used to confirm the lattice structure and inspect for additional phases. Measurements performed at 300 K indicated that all materials studied are nearly single phase and have a tetragonal structure. Some unidentified impurity peaks (about 2–3 %) are observed in the patterns and our attempts to get completely rid of the source of the extra lines were unsuccessful. We also measured the XRD of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ at temperatures below the phase transition at 25 and 180 K using a homemade cryostat.

Magnetic measurements (dc) on solid ceramic pieces were performed at 100 Oe on a commercial (Quantum Design) superconducting quantum interference device magnetometer. The magnetization was measured by two different procedures: (a) The samples were zero-field cooled (ZFC) to 100 K, a field was applied, and the mag-

netization was measured as a function of temperature. (b) The samples were field cooled (FC) from 240 or 340 to 100 K and subsequently the magnetization was measured. The dc temperature-dependent resistance measurements were performed using a standard four-point probe technique, with copper wire contacts attached to each sample with silver epoxy. The external dimensions of the ceramic pieces were not uniform and the results obtained are given in arbitrary units.

MS studies were carried out using a conventional constant-acceleration spectrometer and a 50 mCi $^{57}Co:Rh$ source. The spectra at various temperatures were least-squares fitted with several subspectra corresponding to different iron sites in the materials. The specific heat of a compact piece (about 70 mg) cut from the pellet at $H = 0$ T was measured with a continuous adiabatic heating calorimeter in the range 25–260 K.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Crystal structure

The XRD patterns of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ were taken at 25 and 300 K and the data are presented in Fig. 1. The high-temperature pattern has been determined to be consistent with the characteristic tetragonal $BaNiS_2$ structure, and the lattice parameters obtained [$a = 6.448(3)$ and $c = 8.990(8)$ Å] are in fair agreement with Ref. 1. Within the limits of uncertainty, all $BaCo_{0.85}Ni_{0.15}S_{2-y}$ samples studied have the same lattice constants, confirming that the deficiency of sulfur does not affect the crystal structure. Figure 1 shows that the intensities of the lines at 25 K, corresponding to the (200) and (202) Miller indices, are sharply reduced and broadened compared to those obtained at 300 K, whereas the (003) and (113) peaks remained unchanged. Measurements performed at several temperatures below 180 K show the same trend. This indicates that at the MI transition, there is a slight distortion of the fourfold tetragonal symmetry of $BaNiS_2$ structure. The detailed low-temperature
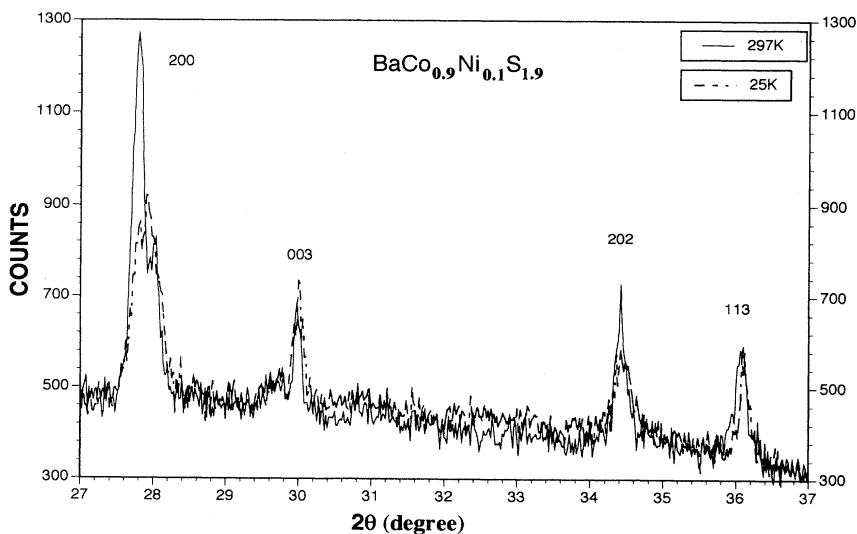

FIG. 1. X-ray-diffraction pattern of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ measured at 25 and 300 K. Note the splitting of the lines corresponding to $hk0$ peaks.

structure is as yet undetermined, and the question whether the symmetry is reduced to twofold orthorhombic or to a monoclinic symmetry with the angle γ larger than 90° (Ref. 7) is now under investigation.

B. Resistivity studies

The temperature dependence of the resistivity (in arbitrary units) for $BaCo_{0.9}Ni_{0.1}S_{2-y}$, where $y = 0$ and $y = 0.1$ is shown in Fig. 2. For $y = 0$ (inset), the resistivity decreases with increasing temperature, indicating semiconducting behavior. On the other hand, the resistivity for $y = 0.1$ exhibits a sharp decrease at $T_s = 220(2)$ K. This change is attributed to the MI transition which occurs for sulfur-deficient samples. Qualitatively speaking, this T_s value is in fair agreement with Ref. 2. However, due to the highly brittleness and porosity of our sample, the drop in the resistivity is much smaller. The increase of the resistivity at low temperatures is probably due to some inhomogeneity of sulfur vacancies, which may mean that in several grains the compound is stoichiometric.

C. Magnetic measurements

The temperature dependence of the susceptibility (M/H) of $BaCo_{0.9}Ni_{0.1}S_{2-y}$ where $y = 0$, 0.1, and 0.2 are shown in Figs. 3 and 4. The main effect to be seen in Fig. 3 is that in $BaCo_{0.9}Ni_{0.1}S_{1.9}$ at the MI transition $[T_s(\text{onset}) = 222$ K$]$, there is a significant decrease in the
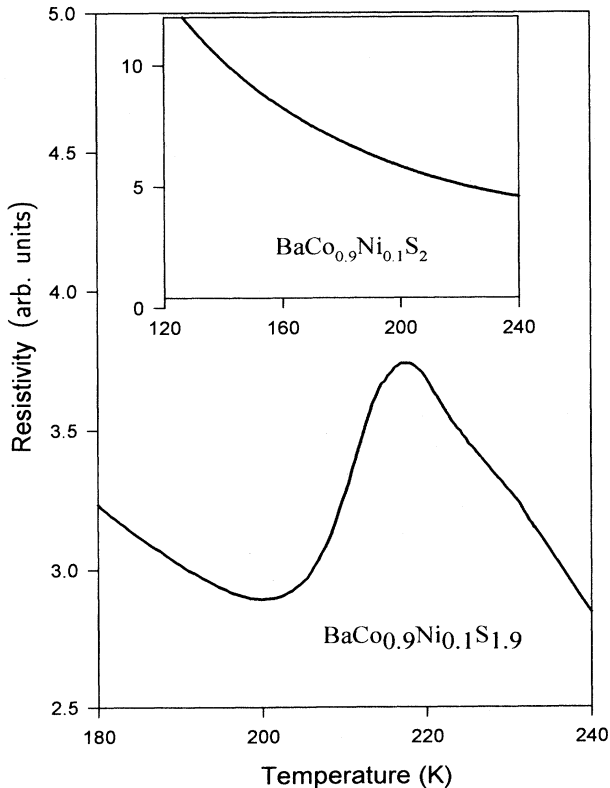
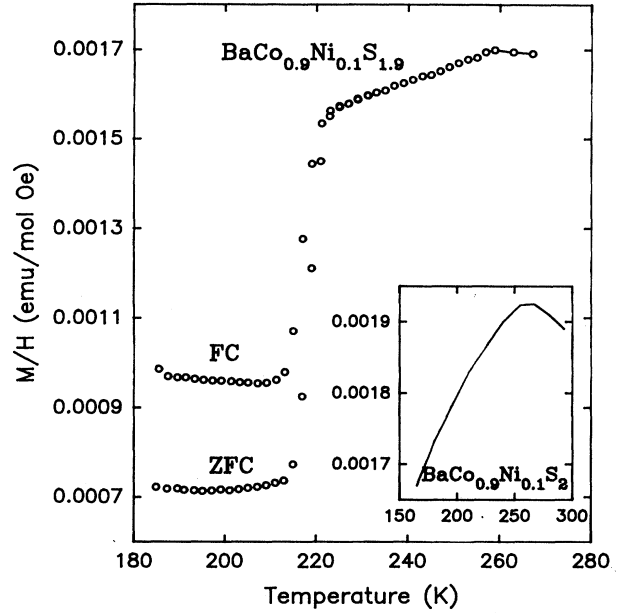FIG. 3. FC and ZFC susceptibility curves for $BaCo_{0.9}Ni_{0.1}S_{1.9}$ and the ZFC curve for $BaCo_{0.9}Ni_{0.1}S_2$.

magnetic susceptibility on going from the insulating phase to the metallic phase. This magnetic transition would provide a reasonable explanation for the observed resistivity anomaly at the same temperature (Fig. 2). Below T_s, the susceptibility is temperature independent, as mentioned above, but a slight increase occurs at about 20 K (not shown) probably due to a small paramagnetic impurity contribution that dominates the low-temperature susceptibility. Above T_s a broad maximum at $T_N = 260(2)$ K is observed. We interpret this as evi-
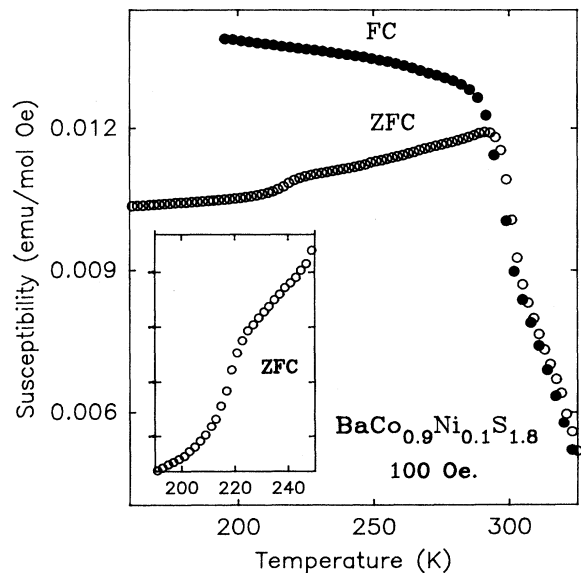
FIG. 2. Resistivity in arbitrary units of $BaCo_{0.9}Ni_{0.1}S_{1.9}$ and of the insulator $BaCo_{0.9}Ni_{0.1}S_2$.

FIG. 4. FC and ZFC susceptibility curves for $BaCo_{0.9}Ni_{0.1}S_{1.8}$. The MI transition is shown in an extended scale in the inset.

dence for two-dimensional antiferromagnetic ordering of the $3d$ Co sublattice in the insulating state. The field dependence of the magnetization curves, measured at 195 and at 230 K (below and above T_s), are linear up to 1 T, and do not show a finite magnetization at $H = 0$ Oe indicating a pure AFM behavior in both regions. For the sake of comparison, the susceptibility of stoichiometric $BaCo_{0.9}Ni_{0.1}S_2$ where a broad maximum is at $T_N = 264(2)$ K is obtained, is also shown (Fig. 3, inset). While the deficiency of sulfur clearly produces a dramatic change in the electrical properties of the system (Fig. 2), the change in T_N is less pronounced.

In order to study the applied magnetic field effect on both the MI and AFM transitions, the FC process was applied on $y = 0.1$ and 0.2 samples. The FC branch in Fig. 3 was obtained while cooling the material at 100 Oe from above T_s and below T_N to 100 K (about 240 K) and recording the magnetization while heating the sample. The two separate branches below T_s indicate clearly that the AFM order persists in the metallic state. For the $y = 0.2$ sample the FC branch was obtained while cooling the sample from about 340 K, and Fig. 4 shows that the higher sulfur deficiency affects T_N and shifts it to 287(2) K, whereas the onset of the MI transition remains at about 220 K. Note that the MI transition is readily observed only in the ZFC branch, because the extra moment obtained in the FC branch masks this transition. The $y = 0.2$ sample contains 0.5 at. % ^{57}Fe and we used this sample also for our specific-heat measurements and the Mössbauer studies presented in the next sections.

The irreversibility in both cases (Figs. 3 and 4) arises from the AFM alignment of the magnetic (Co:Ni) sublattice. It is assumed that in the FC process, during either the MI or the AFM transitions, the external field causes the spins to cant slightly out of their original antiparallel direction. This canting abruptly aligns a component of the moments with the direction of the field and the FC branches are obtained. The FC branch in Fig. 4 is very suggestive of a ferromagnetic alignment occurring at T_N, however, the small difference between the ZFC and the FC branches which accounts for $7 \times 10^{-5} \mu_B$ per formula unit, means that only a tiny fraction of the magnetic spins are affected by the external field.

D. Specific-heat studies

In order to check the thermodynamic properties of the MI transition, we measured the heat capacity of $BaCo_{0.9}Ni_{0.1}S_{1.8}$ in zero applied field (heating rate is 0.3 K/min) and the C_P vs T curve for $25 < T < 260$ K is presented in Fig. 5. The temperature dependence of C_P/T is shown in the inset. The broad anomaly with the peak around 222(1) K is related to the MI transition exhibited in Fig. 4. The entropy associated with this transition amounts to 1.6(1) J/mol K and we shall refer to this value in the discussion. In contrast to the susceptibility data shown in Figs. 4 (inset), where only one broad transition with onset at 230 K is observed, unexpectedly, Fig. 5 shows a second sharp peak around 227 K and its entropy accounts for 0.72(8) J/mol K. For lower heating rate (0.12 K/min) this peak shifts to 240 K and its relative in-
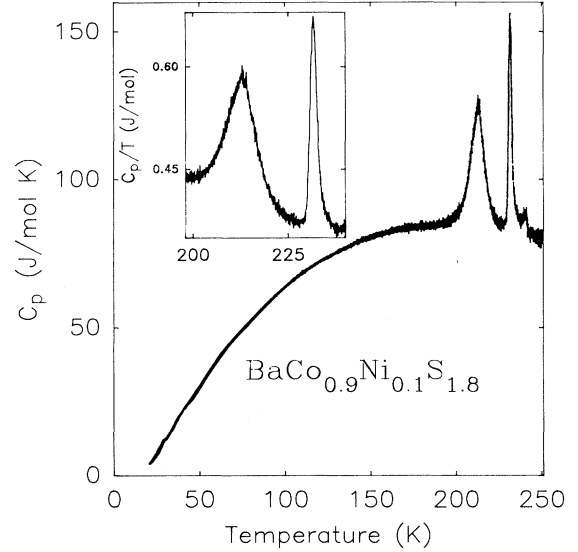

FIG. 5. Specific-heat curve of $BaCo_{0.9}Ni_{0.1}S_{1.8}$ measured at $H = 0$ T with heating rate of 0.3 K/min.

tensity increases, while both the position and intensity of the anomaly related to the MI transition do not change. In the absence of microscopic information, an interpretation of this extra peak is not straightforward. As we shall argue, the MI transition is attributed to a first-order valence transition of Ni^{2+} to Ni^{1+}. It is possible that this transition occurs in two steps not resolved in the susceptibility measurements and a fraction of the entropy is effectively removed above T_s. Note, that a two-step transition was already observed in other systems in which a first-order valence transition occurs.[8] The decrease of C_P at high temperatures ($T > 240$ K) is probably artificial and caused by instrumentation, such as heat leaks from the highly porosive sample to its surrounding.

E. The antiferromagnetism of Co:Ni sublattice: Mössbauer studies

Using Mössbauer spectroscopy (MS) on ^{57}Fe-doped materials, we found the interrelation between superconductivity and AFM in a wide family of cation substitutions in the oxygen-rich Y-Ba-Cu-O system.[5,6] We have shown that the magnetic properties of the high-T_c materials are not affected by the presence of Fe, and that the Fe is a reliable probe of the magnetic behavior of the Cu sites. We use this fact in order to study the magnetic properties of $BaCo_xNi_{1-x}S_{2-y}$. When the Co(Ni) sublattice is magnetically ordered, it produces an exchange field on the Fe located in this site. The Fe nuclei experience a magnetic hyperfine field leading to a six-line pattern in the observed Mössbauer spectra. As the temperature is raised, the magnetic splitting decreases, and above T_N the sextet disappears. We shall present here first MS studies on 0.5 at. % ^{57}Fe-doped stoichiometric $BaCo_{0.9}Ni_{0.1}S_2$, which is semiconducting, AFM at $T_N = 262$ K (Figs. 2 and 3), and in $BaCo_{0.9}Ni_{0.1}S_{1.8}$, which in addition to the AFM order at $T_N = 287$ K, ex-

hibits the MI transition at $T_s = 220$ K discussed above (Figs. 4 and 5).

1. BaCo$_{0.9}$Ni$_{0.1}$S$_{0.2}$

MS studies performed at various temperatures are shown in Figs. 6 and 7. The main information obtained from visual and computer analysis of spectrum measured at 300 K (Fig. 6), is that it is composed of three subspectra corresponding to three inequivalent iron sites (Table I). The reasons for inequivalent Fe sites in this material are as follows. (1) Since Fe is trivalent compared to divalent Co and/or Ni, it attracts sulfur to maintain charge neutrality. It is thus suggested that several sulfur coordinations exist around the Fe ions residing in the Co:Ni sites. (2) Co and Ni are distributed at random over the ($2c$) crystallographic site of the BaNiS$_2$ structure, but their different electronic (magnetic) structures and ionic radii, lead to a distribution in the quadrupole interactions.

The dominant doublet (assigned as I in Fig. 6) which accounts for 43% of the spectral area (Table I), has a quadrupole splitting (QS) of $\Delta = 1/2eqQ = 0.85(2)$ mm/s and an isomer shift (IS) of 0.27(2) mm/s relative to Fe metal. These hyperfine parameters can be assigned to Fe^{3+} in the high-spin state. This doublet is probably related to Fe in the fivefold square-pyramidal coordination of the Co:Ni site described above. This splitting is very similar to the pyramidal configuration ($\Delta = 0.62$ mm/s) obtained for Cu(2) in YBCO.[9] Doublet (II) which has a very small QS [$\Delta = 0.03(1)$ mm/s] may be attributed to a sixfold octahedral coordination for Fe in the $2c$ sites and/or to Fe ions reside in the nonmagnetic Ni position. The configuration of the less intense doublet (III) is not determined. However, this is of little interest in the present paper.

The MS measured at low temperatures (Fig. 7), display additional magnetic splitting that are a clear evidence for long-range magnetic ordering of the Co sublattice. One
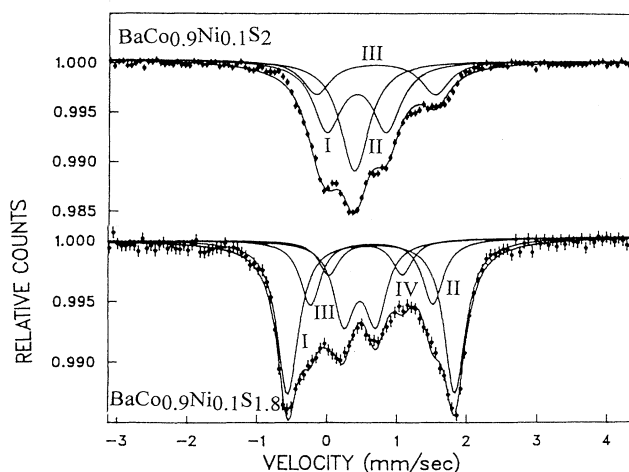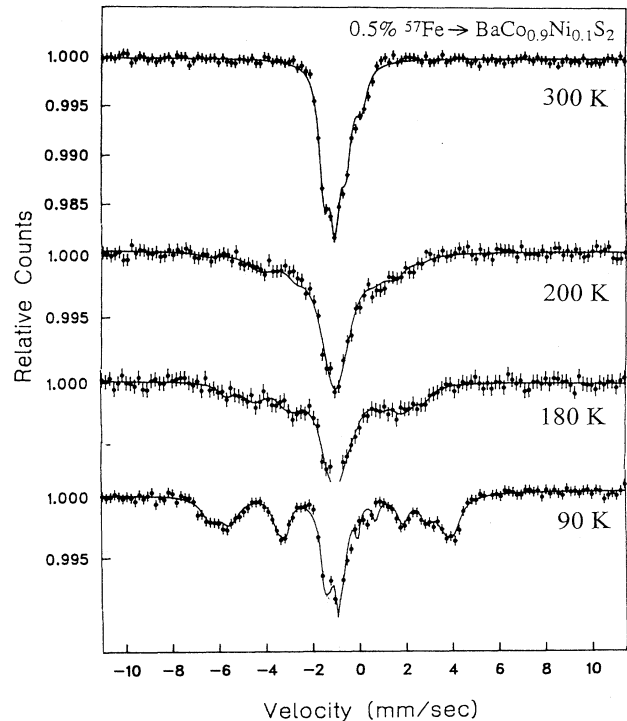

FIG. 7. Mössbauer spectra of 0.5 at.% ^{57}Fe doped in BaCo$_{0.9}$Ni$_{0.1}$S$_2$ at various temperatures.

observes complicated spectra even at 90 K. The major problem confronting any quantitative analysis of these spectra, is the distribution of Fe over the three inequivalent sites where one of them is nonmagnetic and contributes to the doublet in the center of the spectra. We fitted the spectra with consistency to the three subspectra obtained at 300 K (Table I). The hyperfine parameters at 90 K of the nonmagnetic component, which corresponds to doublet II, (35%), are IS$=0.18(1)$ and $\Delta = 0.04(1)$, can be associated with Fe which resides in a nonmagnetic site.

The magnetic hyperfine parameters at 90 K of the two sextets which account for 46% (I) and 21% (II) of the spectral area are $H_{eff} = 287(3)$ and 337(2) kOe, and an effective quadrupole splitting ($1/2eqQ_{eff}$) of $-0.26(2)$ and $-0.73(2)$ mm/s, respectively. The magnetic

FIG. 6. Mössbauer spectra of 0.5 at.% ^{57}Fe doped in BaCo$_{0.9}$Ni$_{0.1}$S$_y$, $y = 0$ and 0.2 at 300 K. Note the extended scale of the spectra.

TABLE I. Hyperfine parameters for the subspectra obtained at 300 K for BaCo$_{0.9}$Ni$_{0.1}$S$_y$, $y = 0$ and 0.2.

BaCo$_{0.9}$Ni$_{0.1}$S$_2$	IS mm/s($\pm$ 0.01)	$\Delta = 1/2eqQ$ mm/s(± 0.02)	Intensity %
I	0.27	0.85	43
II	0.24	0.03	35
III	0.54	1.70	22
BaCo$_{0.9}$Ni$_{0.1}$S$_{1.8}$			
I	0.53	2.38	44
II	0.26	1.00	14
III	0.37	0.40	26
IV	0.69	1.27	16

hyperfine field orientation (θ) relative to the tetragonal symmetry $(c$ axis) given by the relation $1/2eqQ_{eff}=\Delta(3\cos^2\theta-1)/2$ and yields $\theta=69(2)°$ and $77(2)°$, respectively.

As the temperature is raised, the magnetic splitting decreases and disappears at $T>260$ K. The H_{eff} values at 180 K for subspectra (I) and (II) are 205(3) and 268(3) kOe, respectively. Above this temperature, the MS could not be fitted quantitatively because of a distribution of the magnetic hyperfine fields due to a distribution of T_N $(\Delta T_N=30$ K) resulting from inhomogeneity in the sulfur concentration throughout the sample. The spectrum obtained at 270 K (not shown) is very similar to the spectrum shown for 300 K in Figs. 6 and 7.

The probability of a Fe ion to have M Co first-nearest neighbors in $BaCo_{0.9}Ni_{0.1}S_2$ is given by

$$P_M = \begin{bmatrix} P \\ M \end{bmatrix} 0.1^{4-M}0.9^M .$$

We obtain, $P_4=0.65$, $P_3=0.29$, $P_2=0.05$, and $P_1<0.01$. It is therefore clear that only P_4 has to be taken into account, and only Fe ions which have 4 Co ions (or 0 Ni ions) as first-nearest neighbors show observable magnetic splitting.

In conclusion, the MS studies are another direct confirmation of the antiferromagnetic nature of $BaCo_{0.9}Ni_{0.1}S_2$ and agree perfectly with the broad maximum in the magnetic measurements around $T_N=265$ K presented in Fig. 3.

2. $BaCo_{0.9}Ni_{0.1}S_{1.8}$

The motivation of the present paper is to prove directly the presence of magnetic structure in the metallic state, using the MS studies in the whole temperature range. It is noticeable that as the sample becomes sulfur deficient, in addition to the reasons described above, more inequivalent Fe sites exist. We are aware of the fact that MS, especially when several sites are simultaneously present, cannot give unambiguous evidence of the site location. It is shown that depletion of sulfur changes only the sites number, but not the general picture.

A better fit to the MS spectrum of $BaCo_{0.9}Ni_{0.1}S_{1.8}$ is obtained at 300 K (Fig. 6) when four pairs of symmetric doublets are assumed, but with different parameters as in the stoichiometric $BaCo_{0.9}Ni_{0.1}S_2$. The hyperfine parameters of the four doublets are given in Table I.

For $BaCo_{0.9}Ni_{0.1}S_{1.8}$ we obtained $T_N=287$ K (Fig. 4). MS spectra obtained at various temperatures are shown i· Fig. 8. These spectra can be analyzed by using two s.· ttets and two doublets. The distribution of Fe over at least two inequivalent nonmagnetic sites, contributes to the doublets in the center of the spectra, even at 90 K. The hyperfine parameters of nonmagnetic doublets obtained at 90 K with relative intensities (27 and 17%) are similar to those of doublets (III) and (IV) observed at 300 K. The sextets are attributed to Fe ions which replace Co in the $Co(Ni)_2S_2$ planes which order antiferromagnetically. The magnetic hyperfine fields parameters at 90 K of the two sextets, which account for (I) 41% and (II)
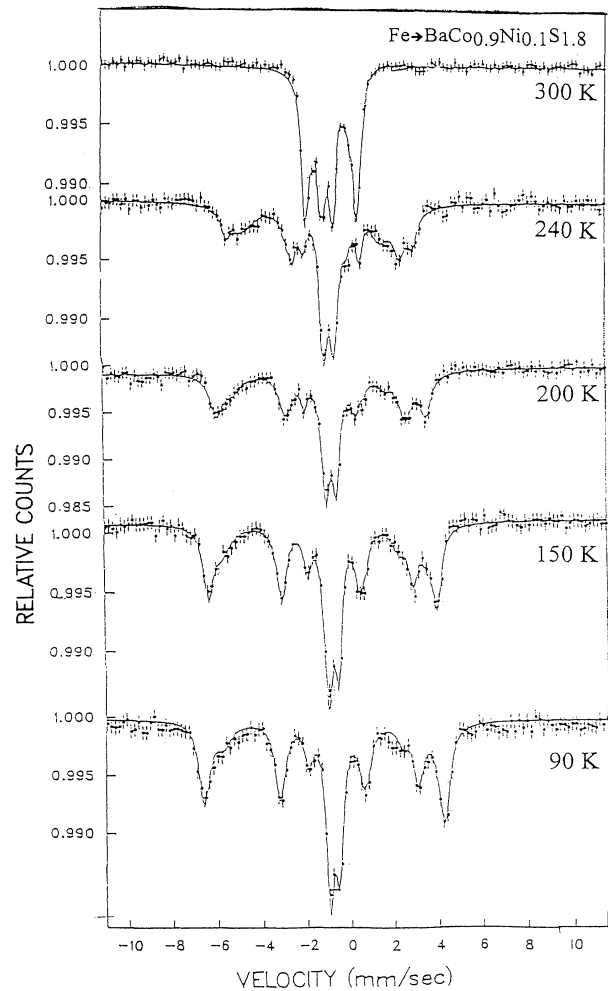

FIG. 8. Mössbauer spectra of 0.5 at. % ^{57}Fe doped in $BaCo_{0.9}Ni_{0.1}S_{1.8}$ at various temperatures.

19% of the spectral area are $H_{eff}=338(3)$ and 314(3) kOe. With $1/2eqQ_{eff}=-1.08(2)$ and $-0.40(3)$ mm/s, respectively. The magnetic hyperfine field orientations (θ) relative to the tetragonal symmetry are $\theta=80(2)°$ and $75°(2)$, respectively. These values are very similar to these obtained for $BaCo_{0.9}Ni_{0.1}S_2$.

As the temperature is raised, the magnetic splitting decreases, and above $T_N=287$ K the sextets disappear. The

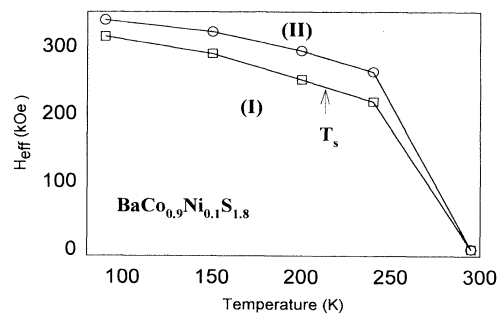FIG. 9. The variation of H_{eff} of the two magnetic sites in $BaCo_{0.9}Ni_{0.1}S_{1.8}$. Note the continuity of values around T_s.

variation of the H_{eff} values as a function of temperature are shown in Fig. 9. Note that below and above T_s the curves are continuous, proving that the magnetic order clearly observed in the insulating state persists in the metallic state without any discontinuity.

DISCUSSION

Our susceptibility measurements of $BaCo_{0.9}Ni_{0.1}S_{2-y}$, are compared to the data reported in Ref. 2. Such a comparison is possible despite the fact that the measurements were performed on samples prepared in different laboratories and therefore have probably a slightly difference in their sulfur content. We both observed two anomalies in the susceptibility curves measured at low applied fields, which are specific to the sulfur-deficient system. Since the semiconducting $BaCoS_2$ is AFM with $T_N = 300$ K,[3] the one distinct peak which is shown in the stoichiometric compounds is associated to the AFM transition of localized spin-$\frac{1}{2}$ Co moments.

In the stoichiometric $BaCo_{1-x}Ni_xS_2$ system, T_N decreases with increasing x. For $x > 0.25$ the samples show metallic behavior and no peak is observed in the susceptibility curves consistent with Pauli paramagnetism of the conduction electrons. Compounds of $Ni^{2+}(3d^8)$ are either diamagnetic in a low-spin state ($S = 0$) when two electrons occupy the $3d_{z^2}$ orbital, or paramagnetic in a high-spin state of $Ni^{2+}(S = 1)$ arising from two unpaired electrons in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals, depending on whether the energy separation of the two uppermost orbitals is greater or less than the energy necessary to cause electron pairing. In most cases and also here in the metallic state (for $x > 0.25$), the energy separation is large and Ni is diamagnetic in the low-spin configuration. The sharp raise of the susceptibility at T_s is attributed to first-order valence phase transition of Ni^{2+} to a monovalent spin-$\frac{1}{2}$ Ni ions. This valence transition to maintain charge neutrality occurs only in sulfur-deficient system. Our MS studies prove that the antiferromagnetic order of

the Co sublattice observed clearly in the insulating state above T_s persists in the metallic state without any discontinuity in the magnetic properties. More precisely, the AFM structure is not affected by the valence transition of Ni.

As a final point of interest we discuss the entropy associated with the MI transition. The calculated entropy value of the valence transition of Ni from $S = 0$ to $S = \frac{1}{2}$ ($x = 0.1$) at T_s which is given by $R \ln 2$ and amounts to 0.6(1) J/mol K, much less than the observed 1.6(1) J/mol K (Fig. 5). This difference can be understood on the basis of a simple argument. As mentioned above, the MI transition is accompanied also by a crystallographic distortion (Fig. 1). Thus, we tend to believe that the extra entropy released (about 1 J/mol K) is due to this phase transition.

Based on studies reported here we can summarize the behavior of the $BaCo_{0.9}Ni_{0.1}S_{2-y}$ system as follows: The system undergoes a first-order MI transition at $T_s = 220(5)$ K and MS studies show that the magnetic order observed above T_s, when the system is semiconducting, persists below T_s in the metallic state without any discontinuity. The MI transition occurs only in sulfur-deficient samples and it is probably caused by a first-order valence transition of Ni ions. In addition, x-ray-diffraction analysis indicate a slight distortion in the tetragonal structure at T_s. Specific-heat measurements show an anomaly at T_s. The entropy associated with the transition 1.6 (J/mol K) is the sum of both valence and crystallographic transitions.

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