Metal-Insulator Transition of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ Induced by Pressure and Carrier Number Control

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In a quasi two dimensional system, BaCoS_2 , the Mott metal-insulator transition can be induced not only by the Ni-substitution for Co but also by the external pressure. Various physical properties have been studied systematically around these Mott transitions. Based on the electronic structure deduced here, the differences between the electronic states near these transitions are discussed in relation to the properties of the anomalous metallic phase of high- T_c oxides.

[$\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$, Mott transition, neutron inelastic scattering, transport properties, thermal properties]

1. Introduction

$\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ consists of alternating stacks of the essentially square-lattice type $\text{Co}_{1-x}\text{Ni}_x\text{S}$ and rock-salt type BaS layers, as shown in Fig. 1, schematically. At $x = 0$, it is in the Mott insulating state and with increasing x or with increasing d -electron number, it exhibits the Mott transition to the metallic state [1-3]. In order to study physical properties of systems which have strongly correlated electrons with low dimensional nature, as the case of high- T_c oxides, we have adopted this compound for systematic studies. Because Co^{2+} ions in BaCoS_2 have been found, as is stated later, to have the spin $s = 3/2$ (high spin), which indicates that at least three 3d orbitals are relevant to its physical properties, in contrast to the essentially single band nature of the high- T_c systems, it has turned out not to be simple to directly compare the properties with those of high- T_c oxides. However, our finding that the Mott metal-insulator (M-I) transition can be controlled not only by the Ni-substitution for Co but also by applying external pressure p [4,5], has presented us an opportunity to comparatively study various physical properties around the Mott transitions induced by the two methods mentioned above.

The present paper briefly surveys results of the experimental studies carried out on both polycrystalline samples [2-8] and single crystals [5,9-11] by various methods. In particular, results of the studies carried out under high pressure are discussed in relation to electronic characteristics of the metallic phase of high- T_c oxides, which is derived from the Mott insulating state by the carrier number control.

2. Experiments

Descriptions of the sample preparation and their characterization can be found mainly in refs. [2] and [3] for polycrystalline samples and in refs. [9] and [10] for single crystals. Measuring methods of the transport, magnetic and thermal properties at ambient pressure have been described in ref [2,3] and [8]. Details of the X-ray and neutron inelastic measurements can be found in refs. [6,7] and [10].

Fig.1. Structure of BaCoS_2 is shown schematically.

Fig.2. Resistivities of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ measured at ambient pressure are shown for various x values. The arrows indicate the T_N values.

Fig. 3. Hall coefficients R_H of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ measured at ambient pressure are shown for various x values.

Fig. 4. Thermoelectric powers S of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ at ambient pressure are shown for various x values.

Details of the studies under high pressure are reported in refs. [5] and [11]. The values of p in neutron and transport measurements cannot always be considered to have accurate correspondence, because different kinds of pressure media were used and, therefore, their T -dependences of p are different. Details can also be found in the papers by Yasui et al. [12] and by Harashina et al. [13].

Fig. 5. Low temperature electric specific heat coefficient γ and the magnetic susceptibility χ of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ at ambient pressure at 10 K are shown as functions of x .

3. Studies at Ambient Pressure

First, experimental results taken at ambient pressure are summarized here. Figure 2 shows the resistivities ρ of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ taken for polycrystalline samples with various x values [3]. The arrows indicate the antiferromagnetic (AF) transition temperatures T_N determined by magnetic susceptibility measurements. The AF ordering disappears with increasing x at $x \sim 0.22$. In the paramagnetic phase, the M-I transition takes place at $x \sim 0.17$. In the AF phase, $d\rho/dT$ is usually negative. (The existence of the AF and metallic phase has been found by recent studies of BaCoS_2 under pressure [12], as is stated later.) The ratio of the resistivities along the directions perpendicular to and within the c -plane was found to be about 10 ~ 50. The persistence of the magnetic scattering ridge along $(1/2, 1/2, l)$ in the reciprocal space up to temperatures far above T_N found by neutron inelastic scattering study [10,11,13] guarantees the two-dimensional nature of the magnetic characteristics.

Figures 3 and 4 show the Hall coefficients R_H and the thermoelectric powers S of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$, respectively [2,3]. In Fig. 5, the low temperature electronic specific heat coefficients γ and the magnetic susceptibilities χ at 10 K of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ are shown. The T -dependences of R_H and S in the x -region near the M-I phase boundary are rather similar to those of electron-doped high- T_c system $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [14,15]. The x -dependence of γ does not decrease, unlike the case of high- T_c systems, as the system approaches the M-I phase boundary from the metallic side. With increasing x to the region far from the phase boundary, R_H becomes T -insensitive and at $x \approx 1.0$, semi-metallic behavior has been found in R_H and S , which is consistent with the vanishing tendency of γ and χ as x approaches unity. (The absolute value of ρ is rather small even at $x \approx 1.0$.)

Figure 6 shows the discontinuity $\Delta\alpha$ found at T_N in the T -

Fig.6. Discontinuity of the linear thermal expansion coefficients, $\Delta\alpha$ of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ at ambient pressure is shown as a function of x . The T_N values are also shown.

dependence of the linear thermal expansion coefficient α as a function of x [8], where T_N values are also plotted. The Ehrenfest relation connects the pressure derivative of T_N with $\Delta\alpha$ as

$$(\partial T_N / \partial p)_{p=0} = 3V_m \Delta\alpha / (\Delta C / T_N),$$

where V_m is the molar volume and ΔC is the discontinuity of the specific heat C at T_N . Then, the change of the sign of $\Delta\alpha$ at $x \sim 0.07$ indicates that the sign of $(\partial T_N / \partial p)_{p=0}$ also changes at the Ni-concentration.

By using these data, we may be able to extract useful information on the electronic state of the present system which has the strongly correlated electrons with two-dimensional nature. The similarity of the anomalous x - and T -dependences of R_H and S to those of high- T_c oxides, found in the x -region near the Mott M-I phase boundary may indicate that there exists a metallic phase which is similar to the anomalous metallic phase (AMP) of high- T_c systems [16,17]. In the case of high- T_c oxides, the strong magnetic interaction plays an important role in the AMP formation. Because the strong magnetic scattering of neutrons which indicates the existence of the two-dimensional spin correlation, has been observed [10] even in the metallic phase of the present system, the anomalous transport behavior may indicate the existence of an AMP in $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$, too. However, neutron diffraction studies [7,10] have shown that the situation is not so simple: The spin of Co^{2+} ions in BaCoS_2 is $3/2$, indicating that at least three 3d orbitals are relevant to the determination of the physical properties of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$. The detailed form factor analyses indicate that these orbitals have the symmetries of $(x^2 - y^2)$, $(3z^2 - r^2)$ and probably $(yz \text{ or } zx)$. This multi-band nature makes it slightly complicated to discuss the physical behavior in relation to that of high- T_c systems.

As an possible electronic structure, which consistently explains the observed behavior, we introduce the one schematically shown in Fig. 7 [7,8]. At $x = 0$, it is in the high

spin ($s = 3/2$) state with the electron configuration of $(3z^2 - r^2)^1(yz \text{ or } zx)^1(x^2 - y^2)^1$. The Ni-substitution for Co adds electrons to the upper Hubbard bands (UHB's) of the $(3z^2 - r^2)$ and/or $(yz \text{ or } zx)$ orbitals. Another effect of the substitution is to induce the upward shift of the $(x^2 - y^2)$ band relative to the $(3z^2 - r^2)$ and $(yz \text{ or } zx)$ bands, which is naturally expected, because the observed semi-metallic and nonmagnetic behavior of BaNiS_2 ($x = 1.0$) indicates that the $(x^2 - y^2)$ is (almost) empty and $(3z^2 - r^2)$ and $(yz \text{ or } zx)$ bands are fully occupied and therefore the $(x^2 - y^2)$ band has a higher energy than those of the $(3z^2 - r^2)$ and $(yz \text{ or } zx)$ bands. The concentration $x \sim 0.07$, where $\Delta\alpha$ changes its sign can be understood as the one, where the lower Hubbard band (LHB) of the $(x^2 - y^2)$ orbitals begins to overlap with the (almost) empty UHB's of the $(3z^2 - r^2)$ and/or $(yz \text{ or } zx)$ orbitals [8]. For details of the consideration on the x -dependence of the electronic structure, see refs. [7] and [8].

We have shown that BaCoS_2 undergoes the Mott transition with increasing Ni-substitution for Co or with increasing 3d electron number and in the metallic phase near the M-I phase boundary, the physical properties often exhibit

Fig.7. Electronic structure of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ is schematically shown. Shaded regions are occupied by electrons. U and L indicate the upper and the lower Hubbard band, respectively.

Fig. 8. $T-p-x$ phase diagram of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$. The abbreviations PI, PM, AFM and AFI mean the paramagnetic insulating, the paramagnetic metallic, the antiferromagnetic metallic and the antiferromagnetic insulating phase, respectively.

rather anomalous behavior similar to that of high- T_c oxides, though the direct comparison is not easy because of the multi-band nature of the present system. For this system, drastic pressure effects have been found on the transport properties as shown in section 4.

4. Studies under High Pressure

The very rapid decrease in the resistivity ρ of the present system with pressure p has been found by Yasui et al. [5]. This phenomenon can be seen over the very wide T -region: For BaCoS_2 , by the application of $p \sim 1.5$ GPa, ρ decreases by factors of $1/300$ and 10^{-7} at 300 K and 77 K, respectively. Now, the insulator to metal transition of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ is known to be controlled by applying relatively small pressure p [4,5,12]. The detailed $T-p-x$ phase diagram of this system is cited in Fig. 8. It is rather similar to that of $(\text{V}_{1-x}\text{M}_x)_2\text{O}_3$ [18] ($\text{M}=\text{Ti}$ and Cr). However, several differences can be found between their transport properties. In $(\text{V}_{1-x}\text{M}_x)_2\text{O}_3$, the transitions from the antiferromagnetic and insulating (AFI) phase to the paramagnetic and metallic (PM) one are of the first order and large hysteresis effects are observed [19], while in the present system, the AFI-PM transition controlled by the applied pressure p is continuous, at least except for $x \sim 0.0$ (see ref. [12] for details). Measurements of the thermal expansion coefficients α of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$ have revealed that the transition at T_N under ambient pressure is of the second order. The critical behavior of various transport quantities is, now, expected to be able to be studied near the second order transitions. Detailed data of the resistivity measurements [5] around the critical pressure of the M-I transition indicate that at $x = 0$, the transition is sharp and probably Mott transition-like, while at $x \neq 0$, it is usually gradual and more or less Anderson transition-like. It can also be said

that in the x -control, the transition is much more gradual than the pressure-induced one of $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$. The antiferromagnetic and metallic (AFM) phase recently found in BaCoS_2 under pressure [12] is also shown in Fig. 8. In the case of the p -control of BaCoS_2 , the electron number of each relevant band of $(x^2 - y^2)$, $(3z^2 - r^2)$ and $(yz \text{ or } zx)$ orbitals does not deviate from unity until the top edge of the LHB of the $(x^2 - y^2)$ orbitals overlaps with the UHB's of $(3z^2 - r^2)$ and/or $(yz \text{ or } zx)$ orbitals, which may be induced with increasing p by the increase of the band width or by the possible upward shift of the $(x^2 - y^2)$ band with respect to the other bands. The occurrence of the sudden carrier number change due to this band overlap can explain the sharp insulator to metal transition with p . However, an alternative mechanism seems to be more plausible. With increasing p , the energy of the electron transfer between the $(x^2 - y^2)$ orbitals gets larger and therefore the effects of the electron correlation becomes weaker, which causes the sudden Mott type transition. If the deviation of the electron number of each relevant band already exists (or if $x \neq 0$), the transition may be smeared out by its effects. The possible evidence for the relevance of the latter mechanism can be found in the results of neutron measurements under pressure. We have performed the form factor analyses of BaCoS_2 in the antiferromagnetic phase both at ambient pressure and at the pressure values near the M-I boundary. The detailed data are shown in refs. [11] and [13]. They show that the spreading of the spin component within the CoS plane observed at the pressures near the M-I phase boundary is significant as compared with that at ambient pressure. It may be considered to be an evidence for the increase of the transfer t of $(x^2 - y^2)$ electrons and supports the picture that the weakening of the electron correlation effect due to this increase of t induces the sharp Mott M-I transition of BaCoS_2 . Then,

Fig. 9. Temperature dependence of the staggered magnetization of BaCoS_2 at ambient pressure (top left), BaCoS_2 at $p \sim 1.5$ GPa (bottom) and $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ (top right) is shown.

Fig.10. Neutron scattering profiles of BaCoS_2 at ambient pressure (top left), BaCoS_2 at $p \sim 1.5$ GPa (bottom) and $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ (top right) measured along $(h, h, -1)$ at $T \sim T_N$ with the energy transfer $E = 3$ meV are shown. The relative intensities can be compared, because they are scaled by using the integrated intensities of the nuclear Bragg reflections.

in contrast to the fact that the substitution-induced Mott M-I transition is driven by the deviation of the electron number per $\text{Co}_{1-x}\text{Ni}_x$ atom, of the relevant band(s) from unity, the pressure-induced one is mainly driven by the decrease of the U/t , U being the intra atomic Coulomb interaction of the relevant orbit. Now, it is interesting to compare characteristics of the dynamical magnetic behavior near the M-I transitions driven by the two methods mentioned above. For this purpose, we measured the magnetic excitation spectra $\chi''(q, \omega)$ of a BaCoS_2 crystal at ambient pressure ($T_N \sim 305$ K) and at $p \sim 1.5$ GPa ($T_N \sim 230$ K : Judging from the phase diagram shown in Fig. 8, T_N should be zero at this pressure value. However, because the p -value was just determined nominally at room temperature, T_N remains finite under this condition. See ref. [12] and [13] for details.), and that of a $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ crystal at ambient pressure ($T_N \sim 180$ K) [10,11,13]. The temperature dependence of the staggered magnetization is shown in Fig. 9, where the arrows indicate the Bohr magneton number per $\text{Co}_{1-x}\text{Ni}_x$ atom (The anomaly observed at ~ 70 K for $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ is due to the structural transition. See ref. 10 for details). For these samples, the scattering profiles along $(1/2, 1/2, -1)$ at $E = 3$ meV were taken under the above pressures and at the temperatures $\sim T_N$. The results are shown in Fig. 10, where the relative intensities can be compared because they are scaled by using the integrated intensities of the nuclear Bragg reflections. It should be added here that both the BaCoS_2 at $p \sim 1.5$ GPa and the $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ at ambient pressure have metallic T -dependence above T_N . Although the T_N values and the low temperature staggered magnetizations of BaCoS_2

at $p \sim 1.5$ GPa and $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$ at ambient pressure are not so different, the inelastic scattering intensities at 3 meV measured at $T \sim T_N$ are quite different, suggesting the significant difference between their electronic state. The metallic state of BaCoS_2 at $p \sim 15$ kbar derived by the weakening of the correlation effects, is expected to have the stronger itinerant nature than $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$. The metallic state derived by the carrier-number control, on the other hand, may still have the strong correlation effects. In other words, the AF state of BaCoS_2 under $p \sim 1.5$ GPa is, we speculate, more spin density wave (SDW) like than that of $\text{BaCo}_{0.82}\text{Ni}_{0.18}\text{S}_2$.

Now, it is interesting to consider the case of high- T_c oxides, which are derived by the carrier number control from the Mott insulating state. In these systems, strong magnetic excitation spectra exist in the low energy region [16,17] even in the superconducting carrier concentration region. The present experimental results are suggestive on the problem what kind of treatment is appropriate to the metallic state of high- T_c systems.

Fig.11. Hall coefficients R_H of BaCoS_2 measured at various p values. The arrows indicate the Néel temperatures T_N .

In $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_2$, it has been shown that R_H and S exhibit anomalous T -dependence which is similar to those observed in the AMP of high- T_c systems [5]. We add here results of R_H -measurements under pressure. Figure 11 show the T -dependence of R_H measured at various values of the applied pressure p . We can see the significant T -dependence even in the pressure region, where T_N vanishes and the system is metallic in all T -region. Because the direct comparison of these anomalous transport properties between the present system and high- T_c oxides should not simply be made, we only give a comment that the magnetic interaction seems to induce this kind of anomalous T -dependence. It is interesting to see the T -dependence of the thermoelectric powers S of BaCoS_2 under pressure.

5. Summary

In quasi two dimensional system BaCoS_2 , it has been found that the Mott insulator→metal transition can be induced not only by the Ni-substitution for Co but also by the application of the external pressure. Various physical properties have been studied around the two kind of Mott transitions. The electronic structure and its x -dependence which can consistently explain the results observed at ambient pressure, has been proposed. Based on the electronic structure, the difference between the two electronic states near the carrier number controlled and pressure controlled transitions has been discussed in relation to the properties of the anomalous metallic phase of high- T_c systems.

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