

Magnetic and transport properties of $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($0 \leq x \leq 0.2$)

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(Received 3 October 1990; revised manuscript received 12 February 1991)

The magnetic and transport properties of BaVS_3 have been studied. The sign of the Seebeck coefficient changed from negative to positive around 70 K when the temperature was decreased. This temperature coincided with the temperature at which not only a metal-semiconductor transition but also a paramagnetic-antiferromagnetic transition were observed. $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($0.0 < x \leq 0.2$) exhibited semiconductive behavior in the temperature range between 70 and 300 K, where BaVS_3 was metallic. We suspected that this change was caused by an Anderson localization of the $3d$ electrons of V ions. It was found that the electrical-conduction mechanism and the species of charge carriers in semiconductive $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ changed, depending on the temperature range.

I. INTRODUCTION

BaVS_3 is known to have a quasi-one-dimensional anisotropic crystal structure which is characterized by linear chains of V^{4+} running parallel to the c axis.¹ Each vanadium ion is located at the center of an octahedron consisting of six sulfur ions. The chains are separated by large barium ions. The interchain vanadium-vanadium distance was determined to be 2.805 Å which was much shorter than the interchain distance (along the a axis) of 6.724 Å.¹ The crystal structure of BaVS_3 at room temperature is hexagonal with space group $P6_3/mmc$. Actually BaVS_3 exhibits a structural phase transition from hexagonal to orthorhombic around 250 K.² The temperature dependence of electrical resistivity of BaVS_3 has a minimum at approximately 130 K.¹ Above this temperature, resistivity tends to decrease with decreasing temperature, exhibiting a metallic behavior. As temperature decreases there is a mild increase in resistivity in the temperature range between 70 and 130 K and a sharp increase, i.e., a semiconductive behavior, in the temperature range between 70 and 4.2 K. Thus BaVS_3 exhibits a metal-to-semiconductor transition around 70 K.

Magnetic susceptibility of BaVS_3 increases with decreasing temperature, i.e., exhibits a paramagnetic behavior, in the temperature range between 70 and 300 K and has a clear peak at approximately 70 K.² Below this temperature, the susceptibility decreases with decreasing temperature. It was concluded from Mössbauer measurements³ for a sample which contained ^{57}Fe substituting for 1% of V ions that a quasi-one-dimensional antiferromagnetic order occurred at this temperature.³ Therefore it is likely that the metal-to-semiconductor transition in BaVS_3 at 70 K is caused by an antiferromagnetic transition rather than a structural phase transition.

The structural, electrical, and magnetic studies of BaVS_3 and $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ in which part of vanadium sites were substituted by titanium which has a $3d^0$ electric configuration was performed late 1970s.¹⁻⁶ Since then, none have been reported for the transport properties of

these sulfides. In this work we prepare BaVS_3 and $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ceramics, and characterize them in terms of electrical resistivity, dc magnetic susceptibility, thermoelectric power, Hall effect, and magnetoresistance.

II. EXPERIMENTAL PROCEDURE

$\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ceramics were prepared for five different compositions with $x=0.0, 0.05, 0.10, 0.15,$ and 0.20 . Samples were synthesized by the following procedure. Highly pure powders of BaCO_3 , V_2O_5 , and TiO_2 were mixed in ethanol for the cation ratio of $[\text{Ba}]:[\text{V}_{1-x}\text{Ti}_x]=1:1$. The mixed powder was calcined at 660°C for 5 hr in H_2S -Ar mixture gas flow and then slowly cooled to room temperature. The resultant powder was ground and the calcination was repeated three times. The calcined powder was pressed into pellets which were again calcined at 660°C for 5 hr in H_2S -Ar mixture gas flow and then slowly cooled to room temperature. The pellets were then heated in evacuated quartz ampoules at 800°C for 20 hr to obtain black ceramics.

Electrical resistivity was measured employing a standard four-probe technique. dc magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design: MPMS). Thermoelectric power measurements were made in the temperature range of 40 K to room temperature applying a temperature difference of ~ 0.3 K. Hall effect measurements were made at 100 K using magnetic fields of ± 10 T and electric currents of ± 50 mA. The size of the samples used for the Hall coefficient measurements was $0.22 \times 2.16 \times 4.29$ mm³. Magnetoresistance was measured employing a standard four-probe technique at 80 K in the range of magnetic field from 0 to 6 T using a constant current of 1 mA. Since a capacitance sensor (LakeShore Cryotronics, Inc.: Model CS-501GR) was used for temperature monitoring in the magnetoresistance measurements, the temperature stability, dT/T , was better than 0.05%.

III. RESULTS

A. BaVS_3

The temperature dependence of electrical resistivity of the present BaVS_3 sample is shown in Fig. 1. The result was similar to that previously reported.¹ The magnitude of resistivity was of the order of $10^{-3} \Omega \text{ cm}$ and the temperature dependence was metallic in the temperature range between 130 and 300 K. That is, there was a minimum in resistivity at 130 K as previously reported.¹ Resistivity slowly increased as temperature decreased from 130 down to 70 K. As temperature decreased further below 70 K resistivity sharply increased. This sharp increase may indicate that a metal-to-semiconductor transition took place around 70 K. As temperature decreased in the temperature range of 25 and 20 K, the rate of the increase resistivity was less than that in the upper temperature range.

The temperature dependence of dc magnetic susceptibility of the present BaVS_3 sample is shown Fig. 2. This result was also similar to that previously reported.² The temperature dependence of susceptibility was Curie-Weiss-like in the temperature range between 70 and 300 K, exhibiting a paramagnetic behavior. At 70 K, a sharp cusp appeared and, at temperatures below 70 K, the susceptibility sharply decreased on cooling, exhibiting a paramagnetic behavior. Susceptibility had a minimum at 25 K and, at temperatures below 25 K, it increased again on cooling.

Thermoelectric power of the BaVS_3 sample was measured in the temperature range between 40 and 300 K. The temperature dependence of Seebeck coefficient is shown in Fig. 3. The Seebeck coefficient at 300 K was relatively large being equal to $-43 \mu\text{V/K}$ which was of the same order of $-54 \mu\text{V/K}$ previously reported by Gardner *et al.*¹ On cooling, (1) the Seebeck coefficient changed the sign from negative to positive around 70 K and the absolute magnitude of the Seebeck coefficient decreased down to 70 K and increased below 70 K. The experimental facts (1) and (2) indicated that there was a

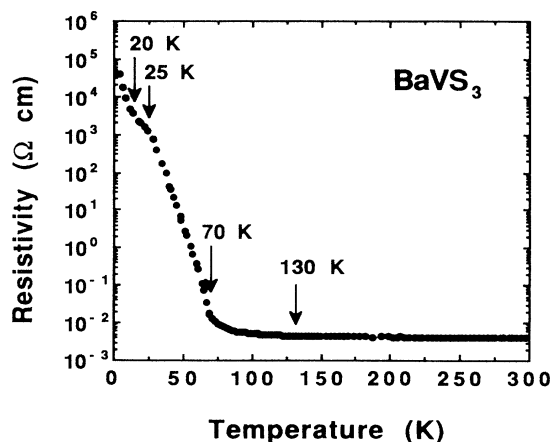


FIG. 1. Temperature dependence of electrical resistivity for BaVS_3 .

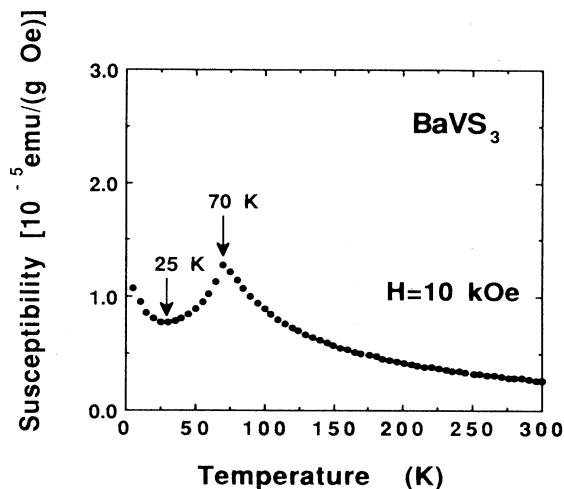


FIG. 2. Temperature dependence of magnetic susceptibility for BaVS_3 .

metal-to-(*p*-type) semiconductor transition around 70 K if a single-band model was employed.

The Hall coefficient, R_H , for BaVS_3 at 100 K was negative being equal to $-2.5 \times 10^{-3} \text{ cm}^3/\text{C}$. If a single-band model is used, the charge carriers are holes, the density of holes being approximately equal to $2.5 \times 10^{21} \text{ cm}^{-3}$.

B. $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$

The temperature dependence of electrical resistivity of Ti-doped samples, $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($0.0 \leq x \leq 0.2$), are shown in Fig. 4. Even with a small amount (5%) of Ti substitution, the metallic portion disappeared and, for $x \geq 0.05$, $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ exhibited semiconductive behavior in the temperature range of 4.2 to 300 K.

The temperature dependence of the Seebeck coefficient for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ in the temperature of 300 to 40 K is shown in Fig. 5. As temperature decreased, $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ exhibited semiconductive behavior in the temperature

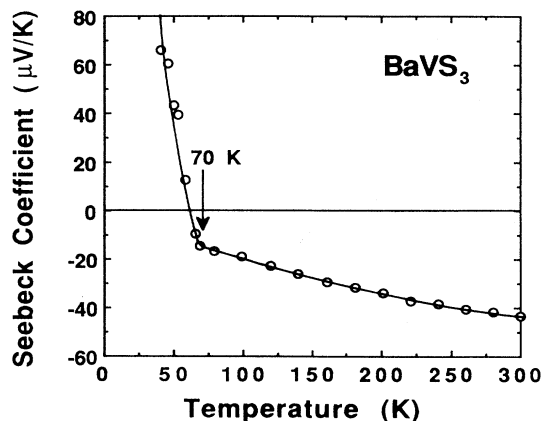


FIG. 3. Temperature dependence of Seebeck coefficient for BaVS_3 .

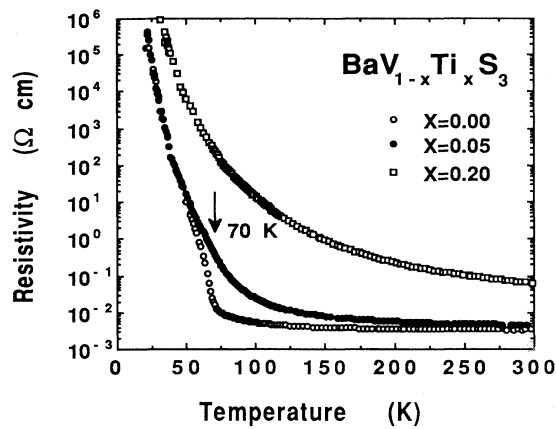


FIG. 4. Temperature dependence of electrical resistivity for $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($x=0.00, 0.05, 0.20$).

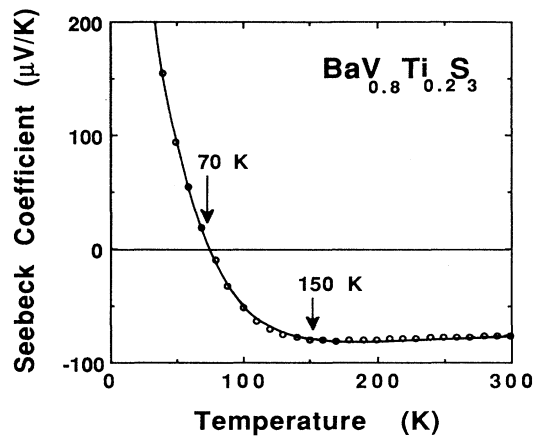


FIG. 5. Temperature dependence of the Seebeck coefficient for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$.

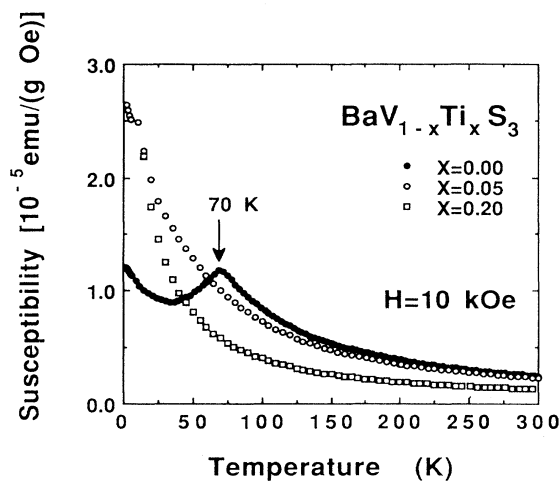


FIG. 6. Temperature dependence of magnetic susceptibility for $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($x=0.00, 0.05, 0.20$).

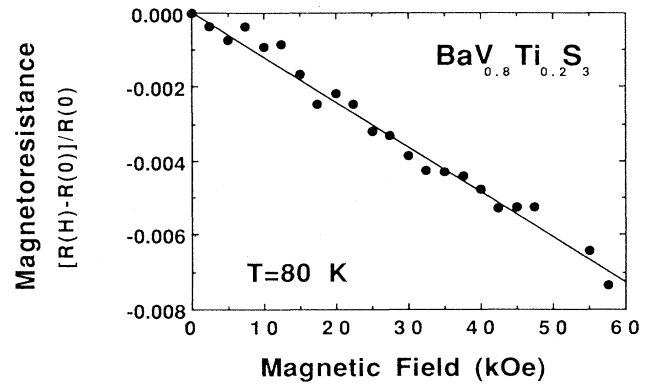


FIG. 7. Magnetic field dependence of resistivity for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$.

ranges between 300 and 150 K and also between 70 and 40 K. If a single-band model was employed, the carriers were electrons in the temperature range of 300 to 150 K, and holes in the temperature range of 70 to 40 K. In the middle temperature range (i.e., between 150 and 70 K), two kinds of carriers could coexist. The Seebeck data were thus not contradictory to the resistivity result shown in Fig. 4 that $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ was semiconductive throughout the temperature range between 40 and 300 K.

The temperature dependence of dc magnetic susceptibility of $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ ($0 \leq x \leq 0.2$) is shown Fig. 6. The antiferromagnetism seems to be destroyed even by 5% Ti substitution for V, and the samples with $x \geq 0.05$ became paramagnetic throughout the temperature range between 4.2 and 300 K. Therefore, the metal-to-semiconductor transition observed around 70 K may be attributed to an antiferromagnetic ordering.

The magnetic field dependence of electrical resistivity of $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ at 80 K is shown in Fig. 7. As the strength of the magnetic field increased, electrical resistivity linearly decreased, and the resistivity in an applied field of 6 T was about 0.7% less than that in zero field, indicating a negative magnetoresistance for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ at 80 K.

IV. DISCUSSION

A. BaVS_3

The previously reported transition around 70 K in BaVS_3 (Refs. 1–3 and 5) was reconfirmed in terms of both resistivity and magnetic susceptibility measurements. Moreover, the Seebeck coefficient measurement supported the existence of such a transition and led us to the conclusion that the transition is not a structural phase transition but a metal-to-semiconductor transition.

From the resistivity data for the temperature range between 4.2 and 20 K, the existence of an impurity level due to excess V is suspected. Using an Arrhenius plot, the depth of the impurity level below the bottom of the conduction band is estimated to be around 1.3 meV. As temperature exceeds 20 K, the electrons from the impuri-

ty level are exhausted until another excitation of electrons (probably for the valence band) starts around 25 K. If this activation process is of the intrinsic semiconductor type, i.e., both electrons and holes are created by thermal activation, the activation energy involved in this process may be estimated to be about 160 meV. Above 70 K, a change in the electronic structure occurs, leading to metallic behavior. Magnetically speaking, when temperature is lower than 20 K, the paramagnetic contribution dominates, while the material is predominantly antiferromagnetic between 25 and 70 K.

B. $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$

Assuming that the susceptibility curve obeys the Curie-Weiss law in the high temperature range, the spin value for the V site was obtained in terms of the Ti content, x , as shown in Fig. 8. In this calculation, the value of 2.0 was employed for Landé's g factor because there were no contributions from the orbital magnetic moment in the $3d$ transition metals. For the sample with $x=0.0$, the spin value was obtained to be 0.31. This value is 62% of the spin when all the V^{4+} ions were assumed to be isolated, i.e., $s = \frac{1}{2}$. As the Ti content, x , increased, the spin value for the V site monotonically decreased and became nearly zero at $x = 0.4$.⁵ On the other hand, it was reported that the phase transition from hexagonal to orthorhombic did not exist for samples with x larger than 0.4.⁴ Therefore, we suspect that there exists a certain relation between the disappearance of spin at the V site and that of the phase transition.

The Ti-content dependence of resistivity and of the spin value may be explained using the model proposed by Massenet *et al.*⁵ as schematically shown in Fig. 9. When all the V ions are isolated, the five fundamental d -wave functions are degenerate. In case of a perfect sulfur octahedral symmetry of the V environment, degenerated wave functions are split into two energy levels, namely, two orbitals (d_{zx} and d_{zy}) in the higher energy level and

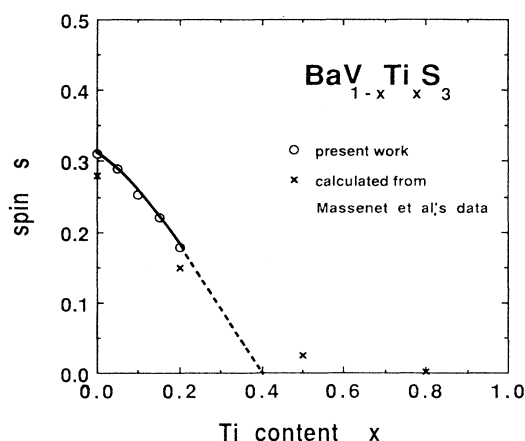


FIG. 8. Variation of spin at the V site in Ti-doped BaVS_3 as a function of titanium content, x : \circ , present work; \times , calculated from the data of Massenet *et al.* (Ref. 5).

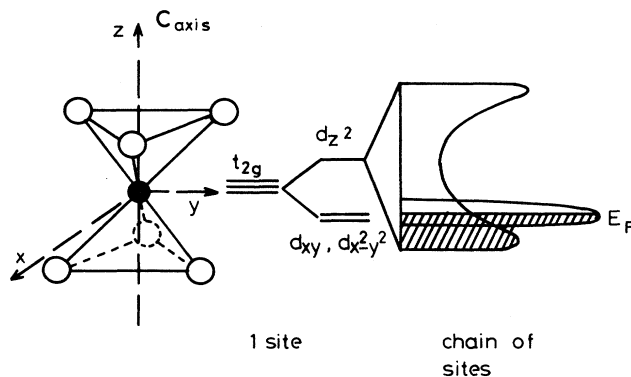


FIG. 9. The model of Massenet *et al.* (Ref. 5) for nearest-neighbor sulfur environment at a vanadium site and corresponding electron level diagrams for one vanadium site as well as for a chain of vanadium sites: \bullet , vanadium atom; \circ , sulfur atom.

three orbitals (d_{z^2} , d_{xy} , and $d_{x^2-y^2}$) in the lower energy level. Since the actual sulfur octahedron extended slightly along the c axis, the orbitals in the lower energy level are split into a fundamental doublet corresponding to two orbitals extending principally in the x - y plane and a higher energy singlet, d_{z^2} . The short distance which separates neighboring V atoms along a single chain leads to a large overlap of the d_{z^2} orbitals so that, in the actual crystal, the d_{z^2} orbital should form a band. The d_{xy} and $d_{x^2-y^2}$ which are actually tilted with respect to the x - y plane also overlap with the nearest neighbor these orbitals,⁶ but to a lesser extent, and should form a narrow band with high density of states. In the d_{z^2} band, the V electrons contribute little to magnetism since they are essentially delocalized. In the d_{xy} and $d_{x^2-y^2}$ bands, the V electrons contribute to magnetism as they are nearly localized. Assuming that the bottom of the d_{z^2} band lies lower than the d_{xy} and $d_{x^2-y^2}$ narrow band in which the Fermi level lies, as shown in Fig. 9, the physical properties of

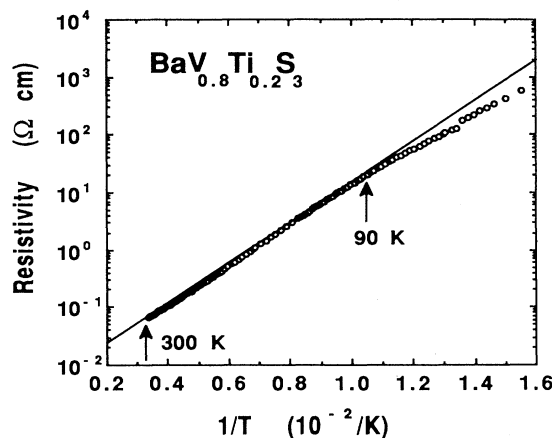


FIG. 10. Log_{10} (resistivity) vs $1/T$ for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$.

$\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ are explained as follows. First, since the spin value at a V site was 0.31 for the sample with $x=0.0$, we infer that about 62% of electrons are in the d_{xy} and $d_{x^2-y^2}$ bands of the sample with $x=0.0$. By substituting progressively Ti^{4+} which have no d electrons, for the V site of BaVS_3 , the number of d electrons decreased and the Fermi level went down and consequently the spin value was decreased. As x gets larger than 0.4, the spin value becomes zero when the Fermi level becomes located under the d_{xy} and $d_{x^2-y^2}$ bands. However, it is impossible with this model to explain how the metallic behavior of BaVS_3 changes to a semiconductive behavior by dilute substitution of Ti for V in the temperature range between 70 and 300 K.

The semiconductive property of $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ at temperatures above 70 K indicated that the carriers were localized by a certain mechanism such as the Mott model⁷ or the Anderson model.⁸ $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ clearly exhibited a negative magnetoresistance, as shown Fig. 7. Thus it is likely that an Anderson localization took place by substituting Ti for the V sites in BaVS_3 .

Electrical resistivity ($\log_{10}\rho$) of $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ is shown as a function of the inverse temperature ($1/T$) in Fig. 10. A curve fitting to the data within a temperature range between 90 and 300 K using the following expression for a thermal activation process:

$$\rho(T) = \rho(0) \exp(\epsilon/k_B T) \quad (1)$$

is shown in Fig. 10, where $\rho(0)$ is a constant and ϵ is the activation energy, k_B is Boltzmann's constant, and T is temperature. The activation energy utilized for the solid line in Fig. 10 was ~ 71 meV. Thus it seems that, in this high temperature range, the major mechanism for the electrical conduction is an activation type. This indicates that the electrons can be excited to the mobility edge which lies ~ 71 meV above the Fermi level when an Anderson localization takes place. The $\log_{10}\rho$ -versus- $(1/T^{1/2})$ plot for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ is shown Fig. 11. The data within a temperature range between 35 and 150 K were fitted to the expression for one-dimensional variable range hopping:⁹

$$\rho(T) = \rho(0) \exp[T(0)/T]^{1/2}, \quad (2)$$

where $T(0)$ is a characteristic temperature. It seems that the major mechanism for electric conduction is one-dimensional variable-range hopping type for Anderson localization with the characteristic temperature of 2.2×10^4 K in this low temperature range. The sample with $x=0.0$ exhibited a metallic behavior. As x increased, the electrons get Anderson-localized because of the introduced randomness. In the low temperature range, electric conductivity was carried by the electrons hopping among the localized states in the valence band.

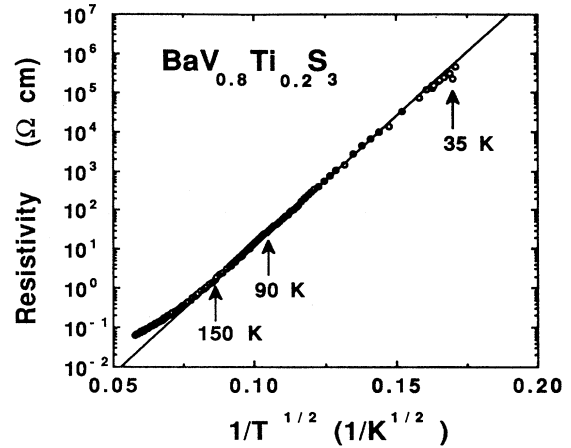


FIG. 11. $\log_{10}(\text{resistivity})$ vs $1/T^{1/2}$ for $\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$.

V. CONCLUSION

From the Seebeck data, it was concluded that the species of charge carriers in BaVS_3 was changed around 70 K from electrons to holes on cooling if a single-band model was employed. That is, the observed metallic behavior in the temperature range between 70 and 300 K was due to electrons, and the semiconductive behavior in the temperature range between 40 and 70 K was due to holes.

$\text{BaV}_{0.8}\text{Ti}_{0.2}\text{S}_3$ exhibited a metal-to-semiconductor transition as x increased, i.e., as the substitution of V proceeded in BaVS_3 . This transition was thought to be caused by an Anderson localization, as evidenced by negative magnetoresistance. It was found that the electrical conduction mechanism for semiconductive $\text{BaV}_{1-x}\text{Ti}_x\text{S}_3$ was different depending on the temperature range. That is, the electrical conduction was carried by a variable-range hopping mechanism in the low temperature range and changed to a thermal activation type at high temperatures. It was also found that the species of charge carriers were depending on the temperature range. Assuming a single-band model, the charge carriers were suspected to be holes in the low temperature range and electrons in the high temperature range.

ACKNOWLEDGMENTS

We are grateful to Professor T. Fujiwara of the University of Tokyo, Dr. T. Ito and K. Kubo of SRL-ISTEC for their helpful discussions. We should also like to thank Professor S. Uchida, Dr. H. Takagi, and H. Eisaki of the University of Tokyo, and T. Kawano of SRL-ISTEC for their help in the Seebeck measurement. We are indebted to S. Koriyama and S. Ikegawa for their kind help in the Hall measurements

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