

# A New Strontium Vanadium Sulfide, SrV<sub>2</sub>S<sub>5</sub>

Norihito Kijima,\* Shōzō Ikeda,† Isao Shimono,‡ Takehiko Matsumoto,† Shigenori Tsuji,§  
Ken-ichi Kumagai,§ and Shoichi Nagata\*<sup>1</sup>

\*Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050, Japan;  
†National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan; ‡Hokkaido Industrial Technology Center, 379 Kikyo-cho,  
Hakodate, Hokkaido 041, Japan; and §Department of Physics, Graduate School of Science, Hokkaido University, Sapporo, Hokkaido 060, Japan

Received February 27, 1996; in revised form May 29, 1996; accepted July 3, 1996

A new strontium vanadium sulfide, SrV<sub>2</sub>S<sub>5</sub>, has been successfully synthesized. The powder X-ray diffraction pattern has been indexed on the basis of a rhombohedral cell with hexagonal lattice constants of  $a = 3.314$  and  $c = 35.023$  Å. However, the electron diffraction measurements show that the structure is more complex and has an unidentified superstructure. The specimens of SrV<sub>2</sub>S<sub>5</sub> show no indication of superconductivity down to 2 K. The resistivity is low, semiconductive, and weakly dependent on temperature above 50 K. The magnetic susceptibility is nearly temperature independent above ~80 K; below 50 K it shows extremely small Curie–Weiss-like behavior. Temperature dependence of the Knight shift in vanadium NMR shows a broad peak around 80 K. © 1996 Academic Press, Inc.

## INTRODUCTION

Since the discovery of high-temperature superconductivity (HTSC), transition metal oxides and sulfides have been studied in order to investigate the mechanism of HTSC and to search for new superconductors. Superconductivity in the copper oxides may be closely related to large quantum fluctuations intrinsic to the  $S = 1/2$  system of Cu<sup>2+</sup> in a two-dimensional crystal structure. When the valence of vanadium ions is 4+, vanadium ions are expected to have  $S = 1/2$ . We focus on vanadium sulfides having  $S = 1/2$ . The vanadium sulfides having  $S = 1/2$  have been considered as candidates for HTSCs, because of the  $(3d)^1$  configuration for V<sup>4+</sup>. A great deal of research is currently devoted to vanadium compounds (1–3).

Studies of SrV<sub>2</sub>S<sub>4</sub> (4) and BaVS<sub>3</sub> (3, 5) have been reported in the Sr–V–S and Ba–V–S systems. SrV<sub>2</sub>S<sub>4</sub> exhibits its metallic behavior and Pauli paramagnetism. SrV<sub>2</sub>S<sub>4</sub> has a complicated hexagonal structure which has the lattice constants  $a = 21.387$  and  $c = 3.332$  Å. BaVS<sub>3</sub> exhibits a metal-to-semiconductor transition on cooling near 70 K.

We have tried to synthesize new sulfides having  $S =$

1/2 in the Sr–V–S system and have succeeded in finding a new strontium vanadium sulfide, SrV<sub>2</sub>S<sub>5</sub>. This sulfide does not exhibit superconductivity down to 2 K. In this paper, we report a method of synthesis for the new compound SrV<sub>2</sub>S<sub>5</sub> using solid state reactions. The crystal structure of SrV<sub>2</sub>S<sub>5</sub> has been determined by analysis of both powder X-ray diffraction and electron diffraction data. The temperature dependence of the electrical resistivity, the magnetic susceptibility, and the Knight shift in vanadium NMR for this new material have been extensively studied.

## EXPERIMENTAL

### 1. Sample Preparation

Three different solid state reactions were examined as part of our effort to produce SrV<sub>2</sub>S<sub>5</sub>. A wide variety of reaction temperatures and times were used to test each reaction route.



Reaction [1], using elemental Sr, V, and S reacted between 500 and 700°C, did not produce SrV<sub>2</sub>S<sub>5</sub>, but rather large amounts of SrS and some unknown impurity phase were produced. Reaction [2], using SrS, V<sub>2</sub>S<sub>3</sub>, and S at 500–1150°C, produced SrV<sub>2</sub>S<sub>5</sub> with many impurity phases. SrV<sub>2</sub>S<sub>5</sub> with fewer impurity phases than reaction [2] was produced by reaction [3], using SrS, V, and S. The details of sample synthesis using reaction [3] are as follows. The starting materials, SrS (purity 99.9%), V (99.9%), and S (99.999%), were mixed in the calculated ratios. After mixing, they were sealed in an evacuated quartz tube with an extra 3 wt% of sulfur and heated to 700°C for a period of 10 days. The resultant powder was ground and pressed into rectangular bars which were again heated to 700°C for 48 h in the evacuated quartz tube. In addition, a higher

<sup>1</sup> To whom all correspondence should be addressed.

TABLE 1  
Result of Compositional Analysis Using EDX<sup>a</sup>

Element	Sr (atomic%)	V (atomic%)	S (atomic%)
Experimental values	11.28	22.78	65.94
	12.36	19.78	67.86
	15.08	26.23	58.69
	15.65	26.77	57.58
	13.32	28.94	57.74
	15.50	29.93	54.57
Average	13.87(1.23) <sup>b</sup>	25.74(2.58)	60.40(3.55)
Calculated values for SrV <sub>2</sub> S <sub>5</sub>	12.5	25.0	62.5

<sup>a</sup> Errors of the measurements are about 10%.

<sup>b</sup> Numerical values in parentheses give the probable errors.

purity specimen was prepared with the initial composition ratio of SrS:V:S = 1:1:2, a composition differing from those of SrV<sub>2</sub>S<sub>5</sub>. Unfortunately, we still have not obtained a single phase specimen of SrV<sub>2</sub>S<sub>5</sub>. Even in the best specimen, small amounts of SrS were detected by powder X-ray diffraction.

## 2. Measurements

The microstructure of the sample was studied with a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The composition of the sample was analyzed with energy dispersive X-ray spectroscopy (EDX). The crystal structure of the sample was characterized by powder X-ray diffraction using CuK $\alpha$  radiation and electron diffraction using a 400 kV electron microscope.

The electrical resistivity,  $\rho$ , was measured by a standard dc four-probe method applying a dc current of 1.0 mA over the temperature range from 4.2 to 300 K. The sintered rectangular bar sample with the dimensions of about  $2.0 \times 1.0 \times 10.0 \text{ mm}^3$  was used for measurements of  $\rho$ .

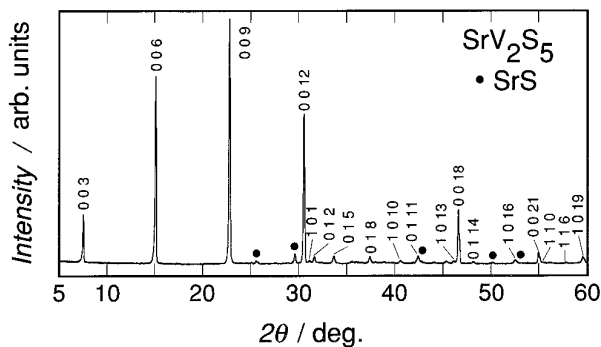


FIG. 1. Powder X-ray diffraction pattern of SrV<sub>2</sub>S<sub>5</sub>. Peaks with solid circles are those of SrS.

TABLE 2  
Indices, Calculated and Observed Values of  $d$  Spacings, and Observed Intensities for SrV<sub>2</sub>S<sub>5</sub> ( $a = 3.314 \text{ \AA}$ ,  $c = 35.023 \text{ \AA}$ )

$h$	$k$	$l$	$d_{\text{obs}}$	$d_{\text{cal}}$	$I_{\text{obs}}^a$
0	0	3	11.731	11.674	18
0	0	6	5.855	5.837	75
0	0	9	3.899	3.891	100
0	0	12	2.922	2.919	59
1	0	1	2.864	2.860	1
0	1	2	2.831	2.832	3
0	1	5	2.657	2.656	3
0	1	8	2.401	2.400	2
1	0	10	2.221	2.220	1
0	1	11	2.132	2.132	3
1	0	13	1.965	1.964	1
0	0	18	1.947	1.946	21
0	1	14	1.886	1.886	1
1	0	16	1.741	1.740	2
0	0	21	1.669	1.668	5
1	1	0	1.657	1.657	<1
1	1	6	1.594	1.594	<1
1	0	19	1.551	1.551	3

<sup>a</sup> It should be noticed that the 00 $l$  peaks are strong because of preferential orientation.

Silver paste (Du Pont No. 4922 thinned with *n*-butyl acetate) was used to fabricate the contacts. The well sintered samples were obtained and the electrical contact was excellent. The dc current was applied in both directions alternately and taking the average values of the observed voltage to compensate for the thermal emf. The magnetic susceptibility,  $\chi$ , which refers to the magnetization divided by a constant field,  $M/H$ , was measured by a Quantum Design SQUID magnetometer in an applied magnetic field of 10 kOe over the temperature range from 2 to 300 K. The powder sample solidified with cyanoacrylate adhesives was used for the measurements of  $\chi$ . Background contribution due to the cyanoacrylate adhesives was subtracted from the experimental result. Vanadium NMR was measured over the temperature range from 4.2 to 400 K. Spectra were obtained by the field-sweep method and the Knight shifts were obtained from the resonance fields.

## RESULTS AND DISCUSSION

The SEM and TEM images of the sample show that the sample consists of small plate-like crystals. The results of the EDX analyses for these plate-like crystals are shown in Table 1. The EDX analyses indicate the composition to be SrV<sub>2</sub>S<sub>5</sub> for several samples within our experimental errors. The powder X-ray diffraction and the electron diffraction patterns of this new sulfide are similar to those of SrNb<sub>2</sub>S<sub>5</sub>, SrTa<sub>2</sub>S<sub>5</sub>, BaNb<sub>2</sub>S<sub>5</sub>, and BaTa<sub>2</sub>S<sub>5</sub> (6–10).

The powder X-ray diffraction pattern of SrV<sub>2</sub>S<sub>5</sub> is shown

TABLE 3  
Lattice Constants and Physical Properties of AM<sub>2</sub>S<sub>5</sub> (A = Sr, Ba; M = V, Nb, Ta)

Compound	Crystal system	Lattice constants		Physical property	References
		$a(\text{\AA})$	$c(\text{\AA})$		
SrV <sub>2</sub> S <sub>5</sub>	rhombohedral	3.314	35.023	semiconductive	present work
SrNb <sub>2</sub> S <sub>5</sub>	hexagonal	3.359	24.00		(6)
SrTa <sub>2</sub> S <sub>5</sub>	hexagonal	3.306	24.28	superconductive ( $T_c \sim 3$ K)	(6, 15)
BaV <sub>2</sub> S <sub>5</sub>	unknown				
BaNb <sub>2</sub> S <sub>5</sub>	hexagonal	3.32	24.88	metallic ( $T > 1.9$ K)	(10)
		3.331	24.72		(6)
BaTa <sub>2</sub> S <sub>5</sub>	hexagonal	3.326	25.21	superconductive ( $T_c \sim 3$ K)	(6–9)

in Fig. 1. The powder X-ray diffraction pattern has been indexed on the basis of a rhombohedral cell with hexagonal lattice constants of  $a = 3.314$  and  $c = 35.023$  Å. The indices assigned are also shown in Fig. 1. Peaks due to SrS are also presented. In addition, some very weak peaks remain unindexed. They are presumably peaks associated with a superstructure of SrV<sub>2</sub>S<sub>5</sub> as well as some unknown impurity phases which will be described below. It can be seen in Fig. 1 that the intensities of the (00 $l$ ) peaks are fairly strong in comparison with those of the other peaks. This fact suggests that SrV<sub>2</sub>S<sub>5</sub> has a layered structure and is preferentially oriented. The indices, the observed and calculated  $d$  values, and the observed intensities are listed in Table 2. Our previous assignment for the Miller indices of the X-ray diffraction pattern in our brief report by N. Kijima *et al.* (11) was incorrect because of the lack of accurate lattice constants. In this paper we propose a set of revised

assignment as shown in Fig. 1 and Table 2, on the basis of improved and refined X-ray and electron diffraction analyses. This powder X-ray diffraction pattern is similar to those of AM<sub>2</sub>S<sub>5</sub> (A = Sr, Ba; M = Nb, Ta) (6–10), except for the large difference in  $c$ . The lattice constants of AM<sub>2</sub>S<sub>5</sub> (A = Sr, Ba; M = Nb, Ta) are summarized in Table 3. As far as we know, BaV<sub>2</sub>S<sub>5</sub> has not been reported.

The electron diffraction patterns of SrV<sub>2</sub>S<sub>5</sub> are shown in Fig. 2. In addition to the strong spots, many weak spots are observed in Fig. 2. All of the strong spots have been indexed on the basis of a rhombohedral cell with hexagonal lattice constants of  $a = 3.2$  and  $c = 35$  Å which give excellent agreement with the cell dimension obtained from the powder X-ray diffraction analysis. The weak spots indicate the presence of a superstructure. The detailed nature of the superstructure has not yet been determined. This electron diffraction pattern is also similar to those of other

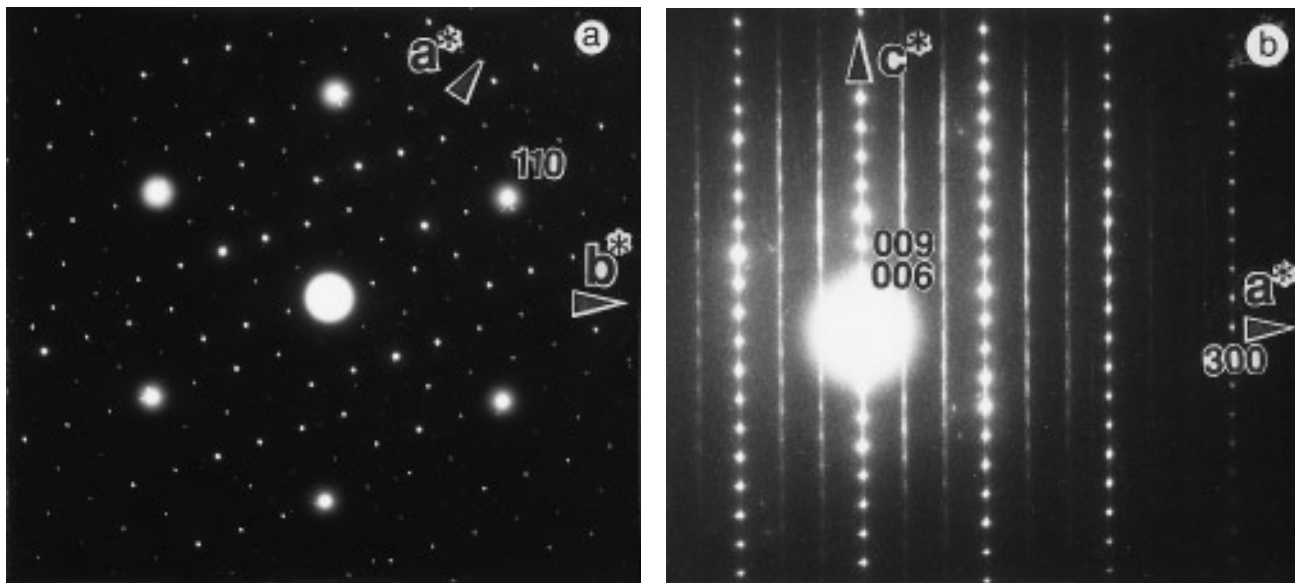


FIG. 2. Electron diffraction patterns of SrV<sub>2</sub>S<sub>5</sub>. The incident beams are parallel to (a) [001] and (b) [010] directions.

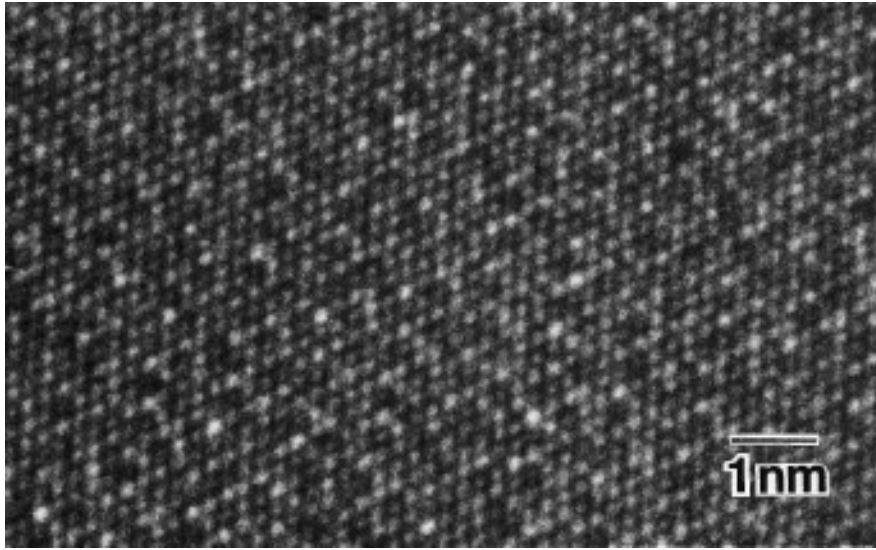


FIG. 3. Lattice image of  $\text{SrV}_2\text{S}_5$ . The beam direction is parallel to [001].

$AM_2\text{S}_5$  compounds ( $A = \text{Sr}, \text{Ba}$ ;  $M = \text{Nb}, \text{Ta}$ ) (6–9). The detailed structure analyses of all these sulfides have not yet been made because of a complicated structure with a superstructure. A lattice image of  $\text{SrV}_2\text{S}_5$  is shown in Fig. 3. The incident beam is parallel to the [001] direction. In Fig. 3, the regular hexagonal cell arrangement which has a cell dimension of about 3 Å is observed. The location of each atom in  $\text{SrV}_2\text{S}_5$  still has not been determined. Detailed structure studies of  $\text{SrV}_2\text{S}_5$  will be published elsewhere (12).

The temperature dependence of the electrical resistivity for a sintered specimen of  $\text{SrV}_2\text{S}_5$  is shown in Fig. 4. The magnitude of the resistivity at room temperature is on the order of  $10^{-2} \Omega \cdot \text{cm}$ . The temperature dependence of the resistivity shows semiconducting behavior. The resistivity is weakly dependent on temperature above 50 K and rises rather rapidly at lower temperatures.

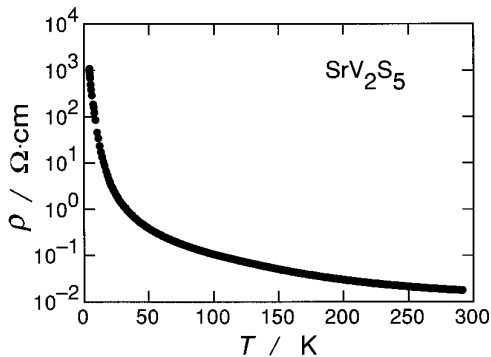


FIG. 4. Temperature dependence of the electrical resistivity for a sintered specimen of  $\text{SrV}_2\text{S}_5$ .

Attempts have been made to fit the electrical conductivity,  $\sigma = 1/\rho$ , versus temperature data to the formula

$$\sigma(T) = A \exp(-q/k_B T), \quad [4]$$

where  $A$  is a temperature independent constant and  $k_B$  is the Boltzmann constant. Figure 5 plots the electrical conductivity as a function of reciprocal temperature  $1/T$ . The experimental result cannot be well reproduced by a single exponential expression in a wide temperature range between 4.2 and 300 K. An activation energy of  $q$  is estimated to be 28 meV in the temperature range between 140 and 300 K.

The temperature dependence of the magnetic susceptibility for  $\text{SrV}_2\text{S}_5$  is shown in Fig. 6. The amount of diamagnetic susceptibility due to the atomic core electrons for  $\text{SrV}_2\text{S}_5$  has been subtracted. The following values are used for the subtraction:  $\chi_{\text{dia.}} = -15(\text{Sr}^{2+}), -6.9(\text{V}^{4+}), -38(\text{S}^{2-}) \times 10^{-6} \text{ emu/mol}$  (13). The magnetic susceptibility is nearly temperature independent above  $\sim 80$  K; below 50 K it shows extremely small Curie–Weiss-like behavior. The magnetic susceptibility,  $\chi$ , has two components: a temperature independent term  $\chi_0$ , and a weak Curie–Weiss-type term. That is,  $\chi$  can be expressed as

$$\chi = \chi_0 + C/(T - \theta), \quad [5]$$

where  $C$  is the Curie constant and  $\theta$  is the asymptotic Curie temperature. Figure 7 plots  $1/(\chi - \chi_0)$  as a function of temperature with  $\chi_0 = 6.0 \times 10^{-4} \text{ emu/mol}$  which may arise from Van Vleck contribution.

The Curie constant,  $C$ , estimated from the solid line in

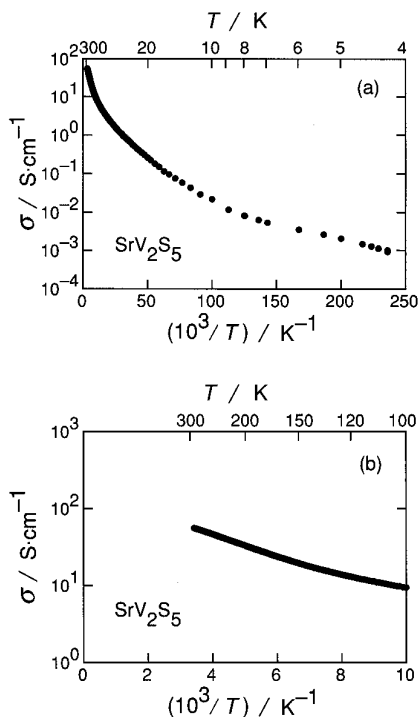


FIG. 5. Electrical conductivity for a sintered specimen of SrV<sub>2</sub>S<sub>5</sub> as a function of the inverse temperature  $1/T$  over a temperature range from (a) 4 to 300 K and (b) 100 to 300 K.

Fig. 7 is  $C = 8.0 \times 10^{-3}$  K emu/mol. Since the magnitude of  $\theta$  is lower than 1 K, the interaction energy between the magnetic moments is considered to be small. Thus, there is neither antiferromagnetic nor ferromagnetic ordering in the temperature region for the experimental data. The effective magnetic moment per vanadium ion from the value of this Curie constant is about  $0.2 \mu_B$  which is much less than the spin-only moment ( $1.73 \mu_B$ ) expected for an isolated V<sup>4+</sup> ion. The magnetic susceptibility increases at lower temperatures. This behavior originates presumably from magnetic impurities.

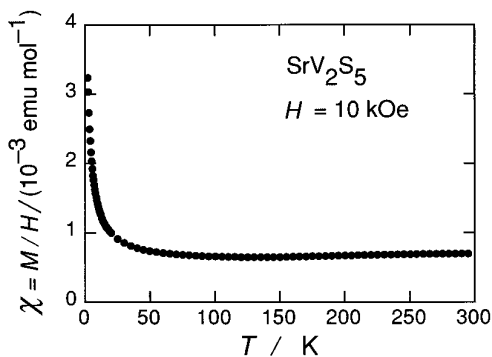


FIG. 6. Temperature dependence of the magnetic susceptibility for SrV<sub>2</sub>S<sub>5</sub>.

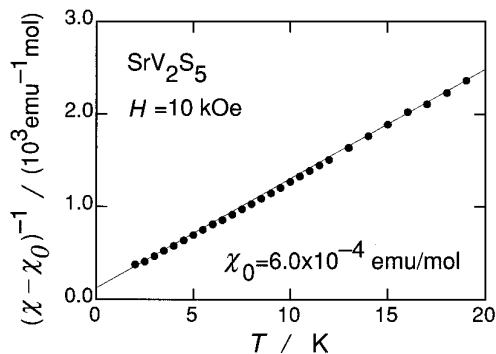


FIG. 7.  $1/(\chi - \chi_0)$  vs temperature for SrV<sub>2</sub>S<sub>5</sub> with  $\chi_0 = 6.0 \times 10^{-4}$  emu/mol. The solid line shows a fitted Curie-Weiss line.

The temperature dependence of the Knight shift <sup>51</sup>V-NMR for SrV<sub>2</sub>S<sub>5</sub> is shown in Fig. 8. The Knight shift is positive and shows weak temperature dependence. This positive Knight shift may be mainly attributed to the contribution from the orbital moment. The Knight shift increases slightly with decreasing temperature down to about 80 K and decreases in the lower temperatures. Whereas the magnitude of the Knight shift varies with increasing temperature above 80 K, the susceptibility keeps constant. The relationship between the temperature dependence of the Knight shift and the susceptibility is not clear at the present. A combined analysis with NMR  $T_1$  measurements is needed. Further detailed NMR experimental results will be reported elsewhere (14).

Physical properties of  $AM_2S_5$  ( $A = \text{Sr, Ba}$ ;  $M = \text{V, Nb, Ta}$ ) are summarized in Table 3. BaNb<sub>2</sub>S<sub>5</sub> is metallic down to 1.9 K (10) and SrTa<sub>2</sub>S<sub>5</sub> and BaTa<sub>2</sub>S<sub>5</sub> exhibit superconductivity around 3 K (6, 9). A study of superconducting properties of SrTa<sub>2</sub>S<sub>5</sub> will be reported (15). On the other hand, SrV<sub>2</sub>S<sub>5</sub> shows semiconducting behavior. Vanadium ions are expected to be tetravalent, assuming Sr<sup>2+</sup> and S<sup>2-</sup> in SrV<sub>2</sub>S<sub>5</sub>. If the valence of vanadium ions in SrV<sub>2</sub>S<sub>5</sub> is 4+, we predict that SrV<sub>2</sub>S<sub>5</sub> has a respectable localized moment due to spin of  $S = 1/2$  in the insulating phase. However, SrV<sub>2</sub>S<sub>5</sub> indicates a disappearance of the localized moment. It is enigmatic that the new compound of SrV<sub>2</sub>S<sub>5</sub> is not metallic but semiconductive and furthermore the disappearance of the localized magnetic moment has undergone in the insulating state. A further investigation is needed to clarify the properties of this new material.

## SUMMARY

A new strontium vanadium sulfide, SrV<sub>2</sub>S<sub>5</sub>, has been successfully synthesized by solid state reaction techniques and its structural, transport, and magnetic properties have been investigated. SrV<sub>2</sub>S<sub>5</sub> has a rhombohedral cell with hexagonal lattice constants of  $a = 3.314$  and  $c = 35.023$  Å. Weak spots in the electron diffraction indicate the pres-

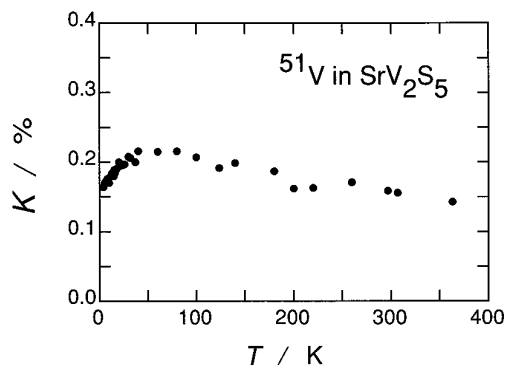


FIG. 8. Temperature dependence of the  $^{51}\text{V}$  Knight shift in  $\text{SrV}_2\text{S}_5$ .

ence of a superstructure.  $\text{SrV}_2\text{S}_5$  shows semiconducting behavior in its transport property and temperature independent susceptibility with an extremely small Curie–Weiss contribution in its magnetic property. Intrinsically the localized moment does not exist in  $\text{SrV}_2\text{S}_5$ . The sign in the shift of  $^{51}\text{V}$ -NMR is positive over the temperature range from 4.2 to 400 K.

#### ACKNOWLEDGMENTS

We thank Mr. H. Nishioka of JEOL (Japan Electron Optics Laboratory) Ltd. for his help with the EDX analysis and the TEM and the electron diffraction measurements. We are grateful to Hokkaido Industrial Technology Center for use of apparatus for the EDX analysis.

#### REFERENCES

1. A. Nozaki, H. Yoshikawa, T. Wada, H. Yamauchi, and S. Tanaka, *Phys. Rev. B* **43**, 181 (1991).
2. F. Deslandes, A. I. Nazzari, and J. B. Torrance, *Physica C* **179**, 85 (1991).
3. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *Phys. Rev. B* **43**, 13118 (1991).
4. W. P. F. A. M. Omlloo, J. C. Bommerson, H. H. Heikens, H. Risselada, M. B. Vellinga, C. F. van Bruggen, C. Haas, and F. Jellinek, *Phys. Status Solidi A* **5**, 349 (1971).
5. R. A. Gardner, M. Vlasse, and A. Wold, *Acta Crystallogr. Sect. B* **25**, 781 (1969).
6. M. Saeki, M. Onoda, and M. Ohta, *Mater. Res. Bull.* **28**, 279 (1993).
7. M. Saeki, H. Nozaki, and M. Onoda, *Mater. Res. Bull.* **24**, 851 (1989).
8. M. Saeki and M. Onoda, *Trends in Inorg. Chem.* **1**, 1 (1990).
9. H. Nozaki, M. Saeki, and M. Onoda, *J. Solid State Chem.* **116**, 392 (1995).
10. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *J. Solid State Chem.* **94**, 294 (1991).
11. N. Kijima, I. Shimono, S. Ikeda, T. Matsumoto, and S. Nagata, "Proc. 8th Int. Symp. on Superconductivity (ISS'95), Advances in Superconductivity VIII/1," (Hayakawa and Enomoto, Eds.) Vol. 1, pp. 433–435. Springer-Verlag, Tokyo 1996.
12. S. Ikeda, in preparation.
13. K. H. Hellwege and A. M. Hellwege (Eds.), "Landort–Börnstein," Group II, Vol. 8, p. 27. Springer-Verlag, Berlin, 1976.
14. K. Kumagai, in preparation.
15. N. Kijima, K. Morie, I. Shimono, and S. Nagata, "Proc. Int. Conf. on Physics and Chemistry of Molecular and Oxide Superconductors," Karlsruhe, Germany, Aug. 1996; *J. Low Temp. Phys.*, in press, 1996.