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Ternary Vanadium Sulfides*,†

T. MURUGESAN, S. RAMESH, J. GOPALAKRISHNAN, AND
C. N. R. RAO‡

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore-560012, India*

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Ternary vanadium sulfides, M_xVS_2 (M = Fe, Co, Ni), with $x = \frac{1}{4}, \frac{1}{3}$, and $\frac{1}{2}$, were prepared and studied. The $x = \frac{1}{4}$ and $x = \frac{1}{2}$ series are isostructural with V_5S_8 and V_3S_4, respectively, while compounds with $x = \frac{1}{3}$ appear to have the hexagonal Cr_2S_3 structure. Structures of NiV_2S_4 and NiV_4S_8 were refined from powder X-ray diffraction intensities. Magnetic and electrical properties reveal that M ions in these sulfides exist in the divalent state having localized moments, while the vanadium $3d$ electrons are itinerant.

1. Introduction

In the vanadium–sulfur system, two stoichiometric phases, VS and VS_2, crystallizing in the NiAs and CdI_2 structures, respectively, are known (*1, 2*). At intermediate compositions, $V_{1+x}S_2$, two ordered phases, V_5S_8 and V_3S_4, corresponding to $x = \frac{1}{4}$ and $\frac{1}{2}$, are known to occur (*1*). These intermediate phases, possessing the NiAs–CdI_2-related structures, may be regarded as metal intercalation compounds in which extra vanadium atoms occupy the octahedral interstices in the van der Waals gap of CdI_2-like VS_2. They may also be regarded as cation-deficient NiAs-type phases consisting of alternating layers fully or partially occupied by cations along the hexagonal c axis. Two-dimensional ordering of cations and vacancies occurs in the partially occupied layers giving rise to different superstructures (*3*). A few of the ternary phases, M_xVS_2, where M is another transition metal, are known (*4–7*). We carried out a systematic study of M_xVS_2 systems with $x = \frac{1}{4}, \frac{1}{3}$, and $\frac{1}{2}$ and M = Fe, Co, and Ni, in an attempt to elucidate the structures and electronic properties of the ordered phases formed in these systems.

2. Experimental

$M_{1/2}VS_2$ were prepared by reaction of the corresponding MV_2O_6 oxides with dry H_2S around 750°C carried out in graphite boats. Sulfidation, which involves the simultaneous reduction of vanadium to the 3+ state, is complete in about 48 hr as indicated by the weight increase according to the reaction

$$MV_2O_6 + 6H_2S \rightarrow MV_2S_4 + 6H_2O + 2S,$$

as well as the weight loss on reoxidation of the sample in air. $M_{1/4}VS_2$ and $M_{1/3}VS_2$

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† Communication No. 148 from the Solid State and Structural Chemistry Unit.

‡ To whom correspondence should be addressed.

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could not be prepared by this method, probably because of the larger S/(M + V) ratios in these phases which could not be obtained by reaction with H_2S. $M_{1/4}VS_2$ phases were prepared by the following method. The mixed oxides with the required M/V ratios were first heated in H_2S around 500°C for 4 days with one grinding in between. The S/(M + V) ratios in the samples at this stage were around 1.45 to 1.5 instead of 1.60 expected for the composition $M_{1/4}VS_2$. The samples were mixed with extra sulfur to bring the composition exactly to $M_{1/4}VS_2$ and the pellets were sealed in evacuated silica tubes and heated at 850°C for 2 weeks. This procedure gave homogeneous crystalline materials with the required composition. A similar procedure was adopted for the synthesis of $M_{1/3}VS_2$ phases. For the purpose of comparison, a sample of NiV_4S_8 was prepared from the elements. X-Ray diffraction patterns of both the preparations were identical.

The M/S ratios and compositional homogeneity of the samples were determined by X-ray microanalysis in an electron microscope (*8*). Characteristic $K\alpha$ emission intensity of the transition metals, together with the SK intensity, were used. Data were collected on 10 random crystals in each sample and the results were averaged. The analysis indicated that the samples were compositionally homogeneous, having the required M/S ratios. For example, Ni/S and Co/S atomic ratios in NiV_2S_4 and CoV_2S_4 were found to be 0.245 ± 0.008 and 0.253 ± 0.007, respectively, by this method.

X-Ray powder diffraction patterns were recorded with a Philips diffractometer, PW1050/70, employing Cu$K\alpha$ or Co$K\alpha$ radiation. For the purpose of structure refinement, intensity data on NiV_2S_4 and NiV_4S_8 were collected at a scan of $\frac{1}{4}$° 2θ per minute in the range $10 < 2\theta < 65°$. Before recording the data, the samples were repeatedly ground to minimize preferred orientation effects. In the case of NiV_4S_8, those reflections which were suspected to be affected by preferred orientation were excluded from the refinement. The methods for the measurement of electrical resistivity, Seebeck coefficient, and magnetic susceptibility were the same as reported earlier (*9*).

3. Results and Discussion

3.1. Crystal Chemistry

We made attempts to prepare M_xVS_2 phases with M = Mg, Mn, Fe, Co, Ni, and Zn for various values of $x < 1$, but we were able to obtain CdI_2-related phases only when M = Fe, Co, and Ni for $x = \frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$. X-Ray diffraction patterns of the $x = \frac{1}{4}$ (MV_4S_8) and $x = \frac{1}{2}$ (MV_2S_4) samples could be indexed on the basis of monoclinic unit cells similar to V_5S_8 and V_3S_4 (*10*). The phases with $x = \frac{1}{3}$ show a hexagonal cell similar to Cr_2S_3 (*11*). Relationships between these supercells and the CdI_2 subcell are as follows:

$$M_{1/4}VS_2\text{: } a_M \approx 2(3)^{1/2}a,\ b_M \approx 2a,\ c_M \approx 2c,$$

$$M_{1/3}VS_2\text{: } a_H \approx (3)^{1/2}a,\ c_H \approx 3c,$$

$$M_{1/2}VS_2\text{: } a_M \approx (3)^{1/2}a,\ b_M \approx a,\ c_M \approx 2c,$$

where a and c refer to the parameters of a CdI_2-like subcell. The unit cell parameters of the M_xVS_2 phases prepared are given in Table I. The unit cell parameters of the MV_2S_4 samples and FeV_4S_8 agree closely with the values reported in the literature (*6*, *12*); the cell parameters of other phases are reported here for the first time. The unit cell volumes of the $x = \frac{1}{4}$ and $x = \frac{1}{2}$ samples vary as Fe > Ni > Co, suggesting that M cation exists in the divalent state in all these phases: $r(Fe^{2+}$: high spin) > $r(Ni^{2+})$ > $r(Co^{2+}$: low spin).

In order to confirm the structures of these phases and their relation to the CdI_2 and NiAs structures, we carried out a structure refinement of NiV_2S_4 and NiV_4S_8 using

TABLE I

UNIT CELL PARAMETERS[a] OF M_xVS_2 (M = Fe, Co, Ni)

Compound	a (Å)	b (Å)	c (Å)	β (°)	Unit cell volume, V (Å)^3
FeV_4S_8	11.41	6.66	11.16	91.6	847.7
CoV_4S_8	11.35	6.62	11.01	91.1	827.0
NiV_4S_8	11.39	6.63	11.20	91.7	845.4
FeV_3S_6	5.771	—	16.76	—	494.5
NiV_3S_6	5.698	—	16.69	—	480.1
FeV_2S_4	5.858	3.298	11.27	92.1	217.6
CoV_2S_4	5.828	3.281	10.92	92.3	208.6
NiV_2S_4	5.842	3.279	11.32	92.2	216.7

[a] The standard deviations are within 0.01 Å and 0.1°.

TABLE II

X-RAY POWDER DIFFRACTION DATA OF NiV_2S_4

d_{obs} (Å)	d_{calc} (Å)	hkl	I_{calc}	I_{obs}
5.54	5.55	002	21.7	23.9
5.25	5.25	$10\bar{1}$	7.7	5.1
5.08	5.09	101	42.3	41.6
2.914	2.919	200	13.7	15.4
2.888	2.859	110	29.9	26.7
2.627	2.625	$20\bar{2}$	14.4	15.0
2.564	2.561	$11\bar{2}$	71.7	74.1
2.550	2.543	202	35.7	34.5
2.529	2.522	112	14.7	17.1
2.453	2.454	013	27.6	26.6
2.128	2.128	211	20.0	17.1
2.049	2.051 2.049	$20\bar{4}$ 105	28.1 10.0	41.6
2.010	2.010	$11\bar{4}$	60.8	57.3
1.972	1.973 1.973	114 204	68.4 29.4	100
1.903	1.904 1.902	301 $21\bar{3}$	10.5 21.4	30.0
1.751	1.750	$30\bar{3}$	12.9	15.3
1.672	1.673	310	51.0	52.2
1.639	1.640	020	30.1	30.0

powder diffraction intensity data and assuming trial structures similar to V_3S_4 and V_5S_8 (*10*). The least-squares program POWDER (*13*) was used for the structure refinement, which minimizes the squares of the differences between the observed intensities and those calculated from the trial model. The residual R obtained in this program is

$$\tfrac{1}{2}[\Sigma\, w(I_{obs} - I_{calc})^2/\Sigma\, w I_{obs}{}^2]^{1/2}.$$

Scattering factors and corrections for anomalous dispersion of Cromer *et al.* (*14, 15*) were employed in the calculations; an overall isotropic temperature factor of zero was assumed in the refinement. The intensity data could be readily refined to low R values and acceptably small standard deviations in the position parameters, indicating the correctness of the trial structures assumed. The observed and calculated intensities for NiV_2S_4 are given in Table II. The refined atomic positions, together with selected bond lengths for NiV_2S_4 and NiV_4S_8, are listed in Tables III and IV. The atomic positions of NiV_3S_6 are given in Table V. It is seen that the Ni–S and V–S bond lengths in NiV_2S_4 are close to the corresponding values of V_3S_4, while the values of NiV_4S_8 are slightly different from those of V_5S_8. In both the compounds, the interlayer Ni–V distances are comparable to the corresponding V–V distances in V_3S_4 and V_5S_8 (*10*).

TABLE III

CRYSTALLOGRAPHIC DATA OF NiV_2S_4

Composition: NiV_2S_4 (Z = 2)
Space group: $I2/m$ (No. 12)

Atom	Position	Atomic coordinates x	y	z
Ni	2(*a*)	0.0	0.0	0.0
V	4(*i*)	0.544(2)	0.5	0.241(2)
S(1)	4(*i*)	0.338(4)	0.0	0.361(3)
S(2)	4(*i*)	0.660(4)	0.0	0.109(2)

Residual factor, R = 3.7%

Selected bond distances (Å)

Ni–S(1)	2.422(4×)	V–S(1)	2.460(3×)
Ni–S(2)	2.336(2×)	V–S(2)	2.330(3×)
Average	2.393		2.395

TABLE IV

CRYSTALLOGRAPHIC DATA OF NiV_4S_8

Composition: NiV_4S_8 ($Z = 4$)
Space group: $F2/m$ (No. 12)

Atom	Position	Atomic coordinates x	y	z
Ni	4(*a*)	0.0	0.0	0.0
V(1)	8(*g*)	0.25	0.312(9)	0.25
V(2)	8(*i*)	0.508(7)	0.0	0.242(5)
S(1)	8(*i*)	0.206(9)	0.0	0.153(10)
S(2)	8(*i*)	0.195(9)	0.5	0.097(9)
S(3)	16(*j*)	0.431(8)	0.246(8)	0.121(7)

Residual factor, $R = 6.6\%$

Selected bond distances (Å)

Ni–S(1)	2.863 (2×)	V(1)–S(1)	2.384 (2×)	V(2)–S(1)	2.716 (2×)
Ni–S(3)	2.454 (4×)	V(1)–S(2)	2.195 (2×)	V(2)–S(3)	2.157 (2×)
		V(1)–S(3)	2.465 (2×)	V(2)–S(3)	2.236 (2×)
Average	2.591		2.348		2.369

X-Ray diffraction data of M_xVS_2 (M = Fe, Co, Ni; $x = \frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$), together with the structure refinement of NiV_2S_4 and NiV_4S_8, confirm that the $x = \frac{1}{4}$ and $x = \frac{1}{2}$ series are isostructural with V_5S_8 and V_3S_4, respectively, while the $x = \frac{1}{3}$ phases are isotypic with Cr_2S_3. It should be noted that the latter structure type does not exist in the binary V–S system (*1*). The structures of all the three series of M_xVS_2, which are related to the basic NiAs/CdI_2 structures, consist of an approximately hexagonal close-packed arrangement of sulfur atoms in which M and V atoms occupy alternating cation layers along the c axis. The cation positions in the V layers are completely occupied, while those in the M layers are partially occupied. Cation ordering for these structures is shown in Fig. 1. From a study of order–disorder transitions in V_5S_8 and V_3S_4, Oka *et al.* (*16*) have shown that the V_5S_8 structure disorders at higher temperatures successively to give V_3S_4, CdI_2, and NiAs structure types. The mechanism suggested for the transformation of V_5S_8 to V_3S_4 structure involves intrachain disordering of cations in the A-type chains of the partially filled layers (Fig. 1b). If the intrachain disordering is restricted to only alternate A chains, the Cr_2S_3 structure results. Therefore, the ordering of cations in the $M_{1/3}VS_2$ phases may be regarded as intermediate between those obtaining in $M_{1/4}VS_2$ (V_5S_8 type) and $M_{1/2}VS_2$ (V_3S_4 type) phases. Similar series of ordered phases have been

TABLE V

CRYSTALLOGRAPHIC DATA OF NiV_3S_6

Composition: NiV_3S_6 ($Z = 3$)
Space group: $R\bar{3}$ (No. 148)

Atom	Position	Atomic coordinates x	y	z
Ni	3(*b*)	0.0	0.0	0.5
V(1)	3(*a*)	0.0	0.0	0.0
V(2)	6(*c*)	0.0	0.0	0.287(4)
S	18(*f*)	0.324(9)	0.052(10)	0.253(2)

Residual factor, $R = 8.1\%$

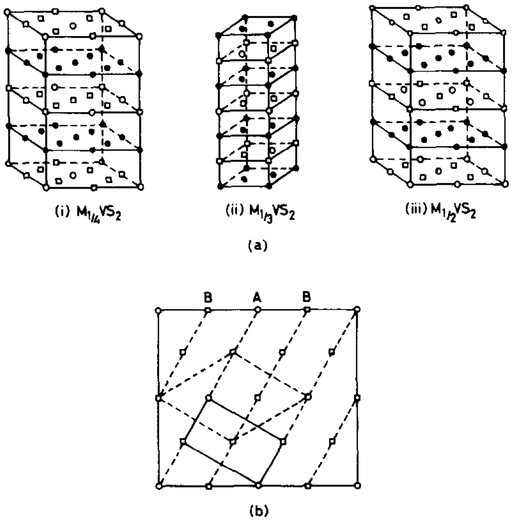

FIG. 1. (a) Structures of M_xVS_2: (i) $M_{1/4}VS_2$, (ii) $M_{1/3}VS_2$, and (iii) $M_{1/2}VS_2$. Only cation layers are shown. Solid circles, V; open circles, M; squares, cation vacancies. (b) Arrangement of cations and vacancies in the partially filled layers of $M_{1/4}VS_2$. The ordering of cations and vacancies for $M_{1/3}VS_2$ and $M_{1/2}VS_2$ is indicated by dotted lines and full lines, respectively. (Partially adopted from Ref. (*3*).)

reported by Takahashi and Yamada in the Fe_xTiS_2 system (*17*).

Our inability to prepare M_xVS_2 phases for M = Mg, Mn, and Zn may be taken to indicate the role of metal–metal bonding in the stabilization of these phases. The d^0, d^5, and d^{10} electronic configurations of these ions may not favor formation of metal–metal bonds. It is also significant that only those metals which form NiAs-type monosulfides give rise to M_xVS_2 phases having the NiAs/CdI_2-related structures.

3.2. Magnetic and Electrical Properties

Magnetic susceptibilities of $M_{1/2}VS_2$ and $M_{1/4}VS_2$ systems were measured in the temperature range 300–80°K and the χ_M^{-1}–T plots for the two series of sulfides are given in Figs. 2 and 3. Among the $M_{1/2}VS_2$ compounds, the iron compound shows antiferromagnetic ordering with T_N = 145°K, the value being close to that reported by Oka *et al.* (*12*). There is no evidence of any magnetic ordering in CoV_2S_4 and NiV_2S_4 down to 80°K. Among the $M_{1/4}VS_2$ compounds, the cobalt compound shows a sharp increase in χ_M around 120°K. The χ_M^{-1}–T plot for this compound is not linear above 120°K, indicating that the ordering is likely to be ferromagnetic. A similar magnetic behavior has been reported for $Fe_{1/3}TiS_2$ (*17*). The effective magnetic moments, μ_{eff}, as well as the paramagnetic Curie temperatures, θ, obtained from linear regions of these plots are listed in Table VI. The data can be interpreted by assuming that the moments mainly arise from the divalent M ions, the vanadium contribution being negligible. This assumption is justified in view of the observations that no localized moments exist in VS_2 (*2*) and that the localized moments of V_3S_4 and V_5S_8 are associated with those vanadium ions occupying the incomplete cation layers (*18*). It is to be noted that the average spin-only moments calculated assuming an ionic formula, viz., $M^{2+}V_2^{3+}S_4$ and $M^{2+}V_2^{3+}V_2^{4+}S_8$, are quite different from the experimental values (excepting in FeV_4S_8).

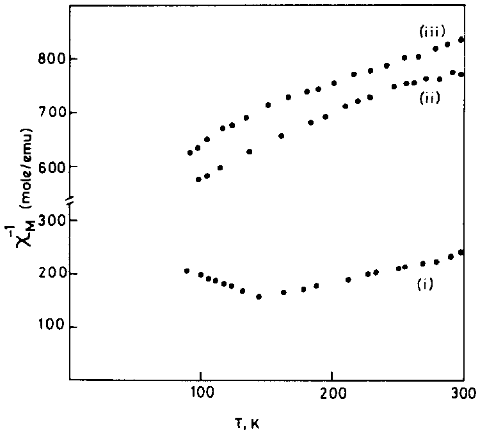

FIG. 2. χ_M^{-1}–T plots of (i) FeV_2S_4, (ii) CoV_2S_4, and (iii) NiV_2S_4.

The μ_{eff} value of FeV_2S_4 (4.85 μ_B) is close to the spin-only moment expected for the high-spin Fe^{2+} ion, while the value of FeV_4S_8 (6.47 μ_B) is much larger. Similar large μ_{eff} values have been reported for $FeTi_4S_8$ (*17*), as well as for $FeNb_3S_6$ and $FeTa_3S_6$ (*19*). In the case of $FeTi_4S_8$, the result has been taken to indicate that iron is present in 3+ (high spin) state, while the

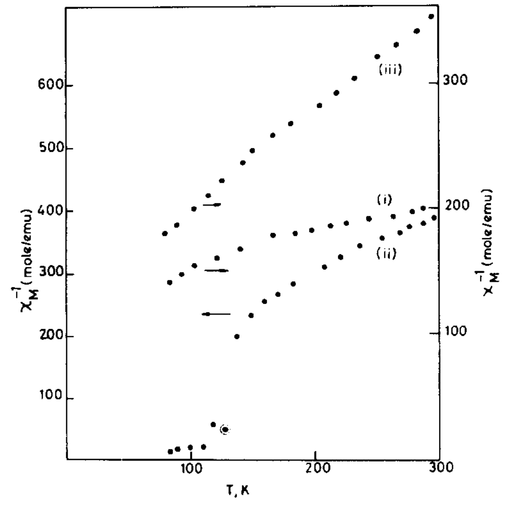

FIG. 3. χ_M^{-1}–T plots of (i) FeV_4S_8, (ii) CoV_4S_8, and (iii) NiV_4S_8.

TABLE VI

ELECTRICAL AND MAGNETIC PROPERTIES OF M_xVS_2 (M = Fe, Co, Ni)

Compound	$\chi_M \times 10^{-6}$ (emu/mole at 300°K)	$\mu_{eff}(\mu_B)$ Expt	Temp. range (°K)	Spin-only moment for $M^{2+}(\mu_B)$	θ (°K)	ρ at 300°K (ohm-cm)	Seebeck coeff. at 300°K (μ_V/deg)
FeV_4S_8	4716	6.47	150–300	4.90	−700	3.4×10^{-3}	+1.7
CoV_4S_8	2413	3.09	160–250	1.73	—	1.2×10^{-3}	−0.2
NiV_4S_8	2932	3.56	150–300	2.83	−280	1.6×10^{-3}	+1.0
FeV_2S_4	4255	4.85	150–300	4.90	−140	12×10^{-4}	+2.8
CoV_2S_4	1302	2.53	100–250	1.73	−350	6×10^{-4}	−0.7
NiV_2S_4	1200	3.14	150–300	2.83	−540	3.3×10^{-4}	−1.5

large moments in $FeNb_3S_6$ and $FeTa_3S_6$ have been attributed to Fe^{2+} with appreciable orbital angular momentum contribution. In view of the instability of octahedral site Fe^{3+} in sulfides, it is likely that the larger moments in these compounds arise from an incomplete quenching of orbital angular momentum of Fe^{2+} ion. The effective moments observed for NiV_2S_4 and NiV_4S_8 are in the usual range reported for octahedral-site Ni^{2+} compounds (*20*). The μ_{eff} values of CoV_2S_4 and CoV_4S_8 are higher than the spin-only value of low-spin Co^{2+}: $3d^7$, but is considerably lower than the value expected for high-spin Co^{2+}. Low-spin Co^{2+} ion shows slightly higher moments in chalcogenides (*21*).

In the MV_2S_4 sulfides, θ varies in the order Fe < Co < Ni, while the trend is opposite in the MV_4S_8 series (Table VI). This is consistent with the result reported by Oka *et al.* (*12*) that the antiferromagnetic state is stabilized in $(Fe_xV_{1-x})V_2S_4$ with increasing iron content, while the reverse happens in the $(Fe_xV_{1-x})V_4S_8$ series.

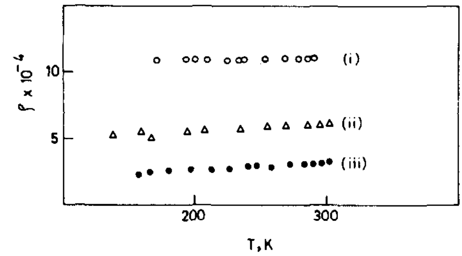

FIG. 4. Temperature variation of electrical resistivity (ρ, ohm-cm) of MV_2S_4 compounds: (i) FeV_2S_4, (ii) CoV_2S_4, and (iii) NiV_2S_4.

All the M_xVS_2 sulfides investigated by us show low resistivities and small Seebeck coefficients (Fig. 4 and Table VI) characteristic of itinerant $3d$ electrons of vanadium. Conduction is definitely metallic in the MV_2S_4 series; resistivities of the other sulfides seem to be at least an order of magnitude higher. Itinerant electron transport is known to occur in many of the metal intercalated disulfides, $M_xM'S_2$, where M' = Ti, Nb, Ta (*22–24*).

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