Magnetic phases of $Fe_xV_{1-x}S$ and their electronic structure

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A study has been made of the $Fe_xV_{1-x}S$ solid solutions with $0<x<0.5$. For the compounds with $x>0.1$, x-ray diffraction analysis discloses a V_5S_8 superstructure. Samples with $x>0.1$ are magnetically ordered at room temperature. The concentration dependences of resistivity and magnetization exhibit sharp peaks for $x=0.1$ and $x=0.2$, respectively. The main features of the structure and electronic properties have been qualitatively explained in terms of the three-band exciton-insulator model, and the maxima in resistivity and magnetization are assigned to the formation of localized magnetic moments with $S=1$, which become delocalized with increasing x. *© 1998 American Institute of Physics.* [S1063-7834(98)02510-6]

Vanadium compounds undergoing a metal-insulator (M-I) transition comprise, besides the well-known oxide series V_nO_{2n-1}, (Ref. 1) also sulfide systems, e.g., V_nS (Ref. 2) and $V_xMn_{1-x}S$ (Ref. 3). The M-I transition in transition-metal oxides and sulfides is accompanied frequently by formation of superstructures in the crystal and magnetic lattices, which are described as charge- or spin-density waves (CDW and SDW, respectively). The CDWs and SDWs are produced also in the course of transformation to the exciton-insulator phase.[4] For instance, the mechanism of the high-temperature M-I transition in vanadium monosulfide VS was considered within the exciton-insulator model.[2]

This work reports on electrical and magnetic measurements and x-ray diffraction and differential thermal analysis (DTA) studies of compounds in the $Fe_xV_{1-x}S$ system with $0<x<0.5$. The electronic structure of these compounds is analyzed.

1. STRUCTURAL DATA

Samples of the $Fe_xV_{1-x}S$ system were obtained by firing a mixture of pure elements at 1200 K for three days in evacuated quartz ampoules. The $Fe_xV_{1-x}S$ compositions prepared by cation substitution of iron for vanadium are as follows: $x=0.01$; 0.02; 0.05; 0.1; 0.2; 0.3; 0.4; 0.5.

X-ray diffraction analysis of the compounds obtained by isomorphic substitution V→Fe in the $Fe_xV_{1-x}S$ system with $0.1\leqslant x\leqslant 0.5$ showed them to be isostructural with V_5S_8 at 300 K.

This served as a starting point in finding the unit cell parameters of our samples. The determination was done by least-squares fitting of 15–30 unambiguously indexed and sufficiently intense reflections chosen throughout the diffraction pattern. The results of the determination are listed in Table I.

DTA curves of $Fe_xV_{1-x}S$ samples placed in evacuated ampoules of a special shape were measured in a MOM derivatograph with a rate of 10 K/min within the 300–1300 K range. All compounds with $0<x\leqslant 0.5$ exhibited two reversible and stable endothermal effects within the 800–900 K interval, which were found earlier[2] to exist in the vicinity of the high-temperature M-I transition in vanadium monosulfide.

The crystal structures formed in the $VS-V_5S_8$ system are based on the high-temperature NiAs hexagonal structure ($B8$ type), which is characterized by the presence on the cation sublattice of randomly distributed vacancies. As the sulfur content progressively increases in going from VS to V_5S_8, one observes an increase in the concentration of vacancies and in the extent of their ordering on the alternating cation layers. The superstructure symmetry changes at 300 K from orthorhombic ($Pmcn$-D_{2h}^{16}) for VS to monoclinic ($F2/m$-C_{2h}^{3}) for V_5S_8.[5]

According to the above x-ray diffraction data, progressive increase of iron concentration in the $Fe_xV_{1-x}S$ system produced from VS brings about formation of a V_5S_8-type monoclinic superstructure for $0.1\leqslant x\leqslant 0.5$, as this is observed in the $V_{1-x}S$ as well.

2. CONCENTRATION DEPENDENCE OF THE MAGNETIC AND ELECTRICAL PROPERTIES

It should be pointed out that the V_5S_8 antiferromagnet ($T_N=30$ K) exhibits metallic conduction, which can occur

TABLE I. Unit cell parameters of $Fe_xV_{1-x}S$ compounds.

	Unit cell parameters, Å			
Composition	*a*	*b*	*c*	β, °
$Fe_{0.1}V_{0.9}S$	11.60	6.61	11.30	90.98
$Fe_{0.2}V_{0.8}S$	11.56	6.60	11.29	91.0
$Fe_{0.3}V_{0.7}S$	11.72	6.62	11.35	91.7
$Fe_{0.4}V_{0.6}S$	11.80	6.60	11.28	91.85
$Fe_{0.5}V_{0.5}S$	11.71	6.60	11.23	92.02
V_5S_8[6]	11.396	6.645	11.293	91.45

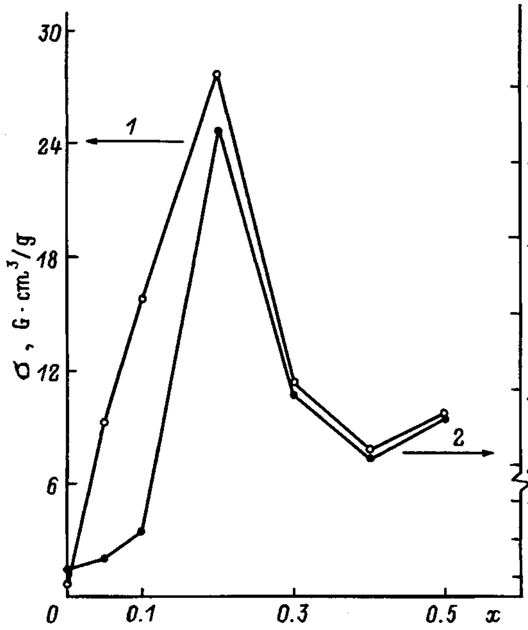

FIG. 1. Concentration dependence of the magnetization σ (curve *1*) and of the average magnetic moment n (curve *2*) per formula unit for the $Fe_xV_{1-x}S$ compounds ($0<x\leqslant 0.5$) measured at 300 K.

with vanadium atoms of two types, namely, with localized and delocalized electrons. The magnetic order is here intermediate between an itinerant antiferromagnet and an antiferromagnet with a localized magnetic moment.[6] Besides, the exciton-insulator model allowing formation of CDWs and SDWs was used to consider compounds with interband electron-hole pairing including the vanadium sulfides and selenides VS, V_3X_4, V_5X_8(X=S, Se).[7]

Figure 1 shows a concentration dependence of the magnetization σ of $Fe_xV_{1-x}S$ samples with $0<x\leqslant 0.5$ (curve *1*) obtained at 300 K. The magnetization was measured on a magnetic balance at room temperature in a field of 13.0 kOe. One readily sees an increase in sample magnetization with increasing iron concentration up to 27.85 G·cm^3/g for $x=0.2$. Subsequent increase of iron concentration in the system for $x>0.2$ results in a decrease of the magnetization to 7.77 G·cm^3/g for $x=0.4$, to be followed by an increase of σ to 9.91 G·cm^3/g for $x=0.5$.

Curve *2* in Fig. 1 plots the concentration dependence of the average magnetic moment in units of μ_B (μ_B is the Bohr magneton) calculated for the formula unit of $Fe_xV_{1-x}S$. A comparison of curves *1* and *2* in Fig. 1 leads to the same conclusion for compounds with $x>0.1$. Besides, assuming the magnetic state of the $Fe_xV_{1-x}S$ samples to be connected only with iron atoms, one has to analyze the concentration dependence of the magnetic moment M per Fe atom in units of μ_B. Reduction of σ (in units of G·cm^3/g) to M (in units of μ_B) showed that the maximum magnetic moment of 2.06 μ_B is observed in this case for the $x=0.2$ composition, with its subsequent decrease to 0.3 μ_B with x increasing to 0.5.

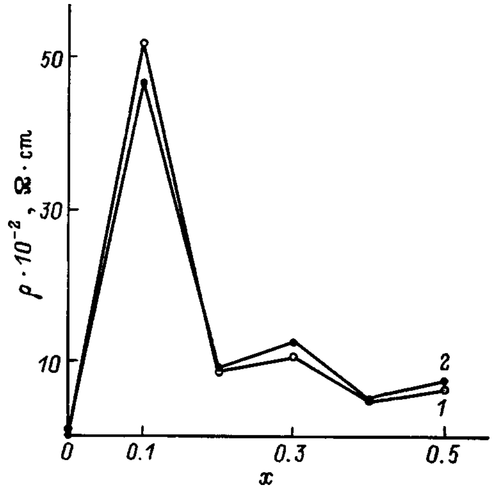

FIG. 2. Concentration dependence of the electrical resistivity $\rho(x)$ of $Fe_xV_{1-x}S$ samples ($0<x\leqslant 0.5$) measured at 300 K (curve *1*) and 80 K (curve *2*).

Figure 2 shows the concentration dependence of the electrical resistivity $\rho(x)$ of $Fe_xV_{1-x}S$ samples with $0<x\leqslant 0.5$ measured at room temperature (curve *1*) and liquid nitrogen temperature (curve *2*). The resistivity measurements were made by the four-probe dc potentiometric method within the 80–300 K interval on parallelepiped-shaped samples annealed at 1000 K in evacuated quartz ampoules. The resistivity is seen to increase steeply at $x=0.1$, followed by a decrease with x increasing to 0.5. At $x=0.1$, the value of $\rho_{300\,K}$ is $50\times 10^{-2}\ \Omega\cdot$cm, and for $x=0.5$ it is $5\times 10^{-2}\ \Omega\cdot$cm, so that the resistivity decreases by an order of magnitude with increasing iron concentration compared to its value at $x=0.1$.

3. ANALYSIS OF THE ELECTRONIC STRUCTURE OF THE $Fe_xV_{1-x}S$ SYSTEM

The analysis starts with the high-temperature hexagonal α phase of VS, which can be successively distorted to obtain both the β VS and V_5S_8 structures. The diagram of one-electron levels of the $V^{2+}(3d^3)$ ion in the hexagonal phase is shown in Fig. 3. The a_1 orbitals are directed along the C axis, and the e_g orbitals lie primarily in the hexagonal plane, where they overlap to a considerable extent with the p orbit-

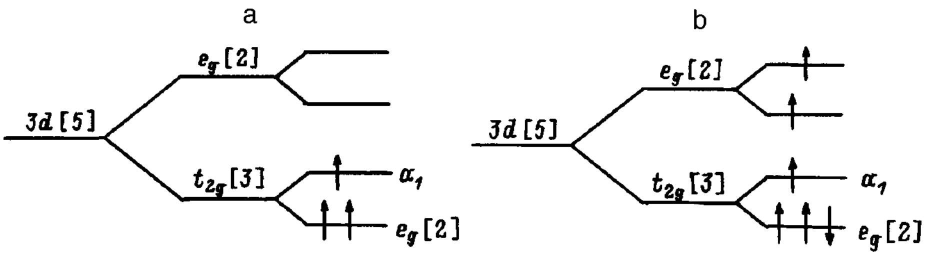

FIG. 3. Diagram of d levels in a crystal field of uniaxially distorted cubic symmetry. The arrows identify the filling of levels for (a) $V^{2+}(d^3)$ and (b) $Fe^{2+}(d^6)$.

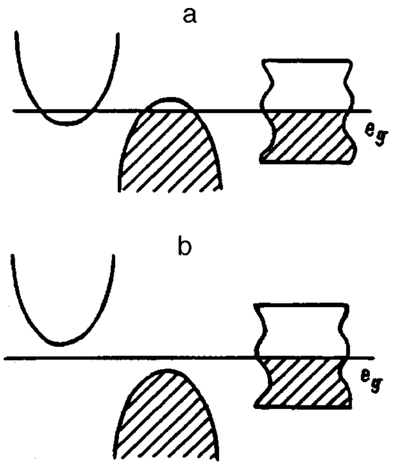

FIG. 4. Electronic structure of VS in (a) hexagonal α phase and (b) orthorhombic β phase.

als of sulfur to form a partially filled e_g band.[8] The overlap along the C axis creates the quasi-one-dimensional a_1 band possessing a nesting property, and it is this that accounts for the electronic transformations observed to occur with decreasing temperature or deviation from stoichiometry. This pattern is supported by Fermi surface calculations[9] which revealed two nearly congruent pieces, an electronic one at the Γ point and a hole one at zone edge (the M point) with a nesting vector $\mathbf{Q}\approx\mathbf{G}/2$, where $\mathbf{G}$ is the reciprocal lattice vector. The e_g band plays the part of an electron reservoir and accounts for conduction in the exciton-insulator phase (Fig. 4).[2]

Because the structure existing for $0.1<x<0.5$ in the $Fe_xV_{1-x}S$ system was found to be close to V_5S_8, consider the electronic structure of the latter in terms of the three-band model of Fig. 4. All nonstoichiometric $V_{1-x}S$ structures form α VS through ordering of successive cation-vacancy layers, including V_5S_8, which has a superstructure with $A=2a$, $B=2b$, and $C=2c$. The cation vacancies affect most strongly the specific a_1 band by breaking the quasi-one-dimensional chains and, to a lesser extent, the electron reservoir, i.e., the e_g band, because of the featureless character of its dispersion. NMR data suggest two types of electronic states for V_5S_8, localized and itinerant.[6]

Considered from a structural viewpoint, the $Fe_xV_{1-x}S$ system has a common feature with $V_{1-x}S$ in that the former has impurity Fe atoms, and the latter, V vacancies. Our data on the structural similarity between these two systems permit a conjecture that Fe atoms order on successive cation planes as the vanadium vacancies do. In electronic structure, however, it should not be close to V_5S_8, because in place of the vacancies it has the a^6 states of Fe^{2+} (Fig. 3b). The partially filled a_1 and e_g orbitals of iron combine with the other orbitals of V and S to form a band structure close to α VS (at high temperatures, in the praphase). The partially filled e_g doublet of the Fe^{2+} ion creates a localized magnetic moment with spin $S=1$. For small x, where impurity Fe atoms may be considered independent, this moment $\mu_{\mathrm{Fe}}=2\mu_{\mathrm{B}}$. A paramagnetic metal with local magnetic impurities could be a suitable model to describe the electronic and magnetic systems. As x increases, however, interaction among the impurities (both RKKY type and superexchange mediated by nonmagnetic cations) will result in their magnetic ordering. Besides, an increase of x entails also increasing overlap of the Fe e_g wave functions, which will give rise to delocalization and reduce the magnetic moment. The increase in magnetization per cell observed by us to occur for small x with a peak at $x=0.2$ corresponding to $\mu_{\mathrm{Fe}}\approx 2\mu_{\mathrm{B}}$ can be assigned apparently to the regime of local magnetic impurities. The decrease of magnetization for $x>0.2$ can be associated with delocalization of the iron e_g doublet. This pattern of the concentration dependence of the magnetic properties correlates also qualitatively with the data on electrical conductivity (Fig. 2), which show the strongest localization of electrons to occur at $x=0.1$.

To conclude, our combined structural, magnetic, and electrical measurements have revealed the $Fe_xV_{1-x}S$ solid-solution system with $0<x<0.5$ to be structurally close to the V_5S_8 superstructure. The concentration dependences of magnetization and resistivity exhibit sharp maxima at $x\sim 0.1$. The three-band exciton-insulator model provides a qualitative explanation for the structural features and electronic properties.

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