MAGNETISM
AND FERROELECTRICITY

Correlation between the Magnetic and Electrical Properties of the $(VS)_x(Fe_2O_3)_{2-x}$ Oxysulfide System

G. V. Loseva, S. G. Ovchinnikov, V. K. Chernov, N. B. Ivanova, N. I. Kiselev, and A. V. Bovina

Kirenskiǐ Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: sgo@post.krascience.rssi.ru
Received July 9, 1999; in final form, October 5, 1999

Abstract—The correlation between the magnetic and electrical properties of the $(VS)_x(Fe_2O_3)_{2-x}$ ($0.9 < x < 1.25$) oxysulfide solid solutions has been studied. The crossover of conductivity from the semimetallic to semiconducting type is accompanied by changes in the magnetic susceptibility, which are characteristic of the transition from delocalized to localized electrons. For $x = 1.25$, a region of the ferromagnetic ordering has been established in the temperature range 90–120 K. © 2000 MAIK "Nauka/Interperiodica".

The observation of a colossal magnetoresistance in $La_{1-x}Ca_xMnO_3$ doped manganites has raised interest in other magnetically ordered materials, in which a change in the magnetic properties is accompanied by changes in the electrical ones, namely, by a reversal of the conductivity type and a sharp increase in the magnetoresistance.

The magnetically ordered mixed $3d$-metal compounds, among which are the $Me^IMe^{II}A$ and MeA^IA^{II} doped chalcogenides (Me is $3d$ metal, and A = S or Se), chalcogenide spinels, e.g., $M_{1-x}Cu_xCr_2Se_4$ (M = Zn, Ca, or Hg), and the $(MeO)_x(MeA)_{1-x}$-type compounds, exhibit a broad spectrum of exchange interactions and electrical properties [1]. By varying the composition of these compounds, as well as by properly changing external factors (temperature, electric and magnetic fields, irradiation, etc.), one can tailor new materials to the desired physicotechnical requirements, as well as make possible such phenomena as the photomagnetic effect, the metal–insulator transition, the onset of the ferromagnetic state in an antiferromagnetic phase, etc. In view of the specific features of their electronic and magnetic states, these mixed magnetically ordered $3d$-metal compounds deserve comprehensive experimental and theoretical investigations.

This work reports the results of investigations into structural, thermal, electrical, and magnetic properties of the $(VS)_x(Fe_2O_3)_{2-x}$ oxysulfide system with a spinel structure of the Fe_3O_4 magnetite type.

1. SAMPLE PREPARATION

Polycrystalline samples of the $(VS)_x(Fe_2O_3)_{2-x}$ oxysulfide system with compositions in the range $0.9 < x < 1.25$ were prepared by sintering the appropriate amounts of vanadium monosulfide VS and oxide

α-Fe_2O_3 in evacuated silica tubes at 1100 K for three days, with subsequent cooling at a rate of 40 K/h.

The vanadium monosulfide VS was prepared by annealing of pure, electrolytically produced vanadium metal and 99.999%-pure sulfur in evacuated silica tubes at 1200 K for three days. The monosulfide thus obtained had at 300 K the β-VS structure (MnP type, P_{mcn}, D_{2h}^{16}).

The finely dispersed powder of α-Fe_2O_3 hematite was prepared as the final product of the dehydration of synthesized iron α-hydroxide (α-FeOOH-goethite) by calcination at 558 K. The α-Fe_2O_3 thus obtained had an Al_2O_3-type structure (D_{3d}^6, $R3C$) with the unit cell parameters corresponding to the tabulated values for the α-Fe_2O_3 hematite at 300 K. The dehydration temperature of α-FeOOH was derived from the differential thermal analysis (DTA) data. Besides, the Mössbauer spectra of our α-Fe_2O_3 hematite yielded the estimate $H_{eff} = 515.5$ kOe, which likewise is in agreement with the tabulated value for α-Fe_2O_3 at 300 K.

2. EXPERIMENTAL TECHNIQUE

The X-ray diffraction patterns of the samples were recorded on a DRON-3 diffractometer with CuK_α radiation at 300 K. The X-ray diffraction pattern of the sample with $x = 1.25$ was also obtained at 120 K.

DTA curves were measured with a MOM derivatograph in the range 300–1400 K at a rate of 10 deg/min. The powder samples of the oxysulfides under study were placed in specially-shaped evacuated silica tubes. For each composition, the DTA curves were obtained in three to five heating–cooling runs.

The electrical resistivity ρ was measured by the four-probe dc potentiometric method in the range 77–300 K. The parallelepiped-shaped pressed-powder samples $10 \times 5 \times 3$ mm in size were annealed in evacuated silica tubes at 1300 K for 1 h.

The temperature behavior of the real part of the initial magnetic susceptibility χ' was studied on a setup comprising an inductance bridge and a phase-sensitive detector in the range 77–300 K. The measurements of χ' were carried out on oxysulfide powders placed in a special container 2 mm in diameter and 15 mm long. The powders used in the $\chi'(T)$ measurements were then pressed into the samples for the $\rho(T)$ studies.

3. RESULTS

3.1. X-ray diffraction analysis. X-ray diffraction analysis of the $(VS)_x(Fe_2O_3)_{2-x}$ system with compositions $x = 0.9$, 1.1, and 1.25 showed that at 300 K the samples have a 90–95% spinel structure of the FeO · Fe_2O_3 magnetite type (H_1; O_h^7–$Fd3m$) with a similar cubic-lattice parameter ($a \sim 8.39$ Å [2]). No additional clearly pronounced phases were revealed. The earlier measurement [3] made for $x = 1.0$ showed a sulfospinel phase with a Fe_3O_4-type structure that constituted up to 80%. It was found that the cooling of the sample with $x = 1.25$ from 300 to 120 K is accompanied by structural changes with a lowering of the symmetry. Note that the electronic transition in Fe_3O_4 (the Verwey transition at $T_v = 119$ K) with a decrease in the temperature $T < T_v$ is accompanied by a small orthorhombic lattice distortion of ~0.05% [2]. Above T_v, the Fe^{2+} and Fe^{3+} ions randomly occupy the octahedral sites, and below T_v, they are ordered.

3.2. Differential thermal analysis. The DTA curves revealed a reversible endothermic effect for all the compositions at $T \sim 880$ K, which, by analogy with the DTA curves obtained for the Fe_3O_4 magnetite and FeS · Fe_2O_3 sulfomagnetite (the endothermic effects at 830 and 850 K correspond to the Curie temperatures T_c), can be identified with the Curie points of the vanadium oxysulfides. Besides, the T_c temperature for the $(VS)_{1.0}(Fe_2O_3)_{1.0}$ composition prepared by sintering equimolar amounts of the monosulfide and oxide, which was derived earlier from magnetic measurements and the corresponding DTA endothermic peak, is approximately 870 K [3].

The DTA curves of the compositions studied yielded a melting temperature of 1340 K for $x = 0.9$, which increases to 1370 K for $x = 1.25$.

3.3. Electrical properties. Figure 1 presents the logarithm of the resistivity as a function of temperature, $\log[\rho(T)]$, plotted for the compositions $x = 0.9$, 1.1, and 1.25 in the range 77–300 K. One can readily see that the $\log[\rho(T)]$ dependences for $x = 0.9$ and 1.1 at temperatures from 80 to 240 K have semiconducting character, and at $T > 240$ K, the oxysulfide with $x = 0.9$ undergoes

a smooth crossover from the semiconducting to semimetallic type of conductivity. The composition with $x = 1.1$ in the range 240–280 K exhibits a decrease in the resistivity by about an order of magnitude with the activated character of conductivity retained up to 300 K. Earlier measurements for the composition with $x = 1.0$ revealed a decrease in ρ by a factor of seven or eight in the range 280–330 K, with activated conductivity persisting above 350 K [3].

It is also seen from Fig. 1 that the temperature behavior $\rho(T)$ for samples with $x = 0.9$ and 1.1 has an activated character in the range 160–240 K, whereas for $x = 1.25$, the conductivity is semimetallic. According to [4], such a concentration behavior of the curves for the oxysulfide system under study is characteristic of disordered systems with a concentration-driven Anderson-type metal–insulator transition at a critical concentration x_c. Note that the concentration $x_c = 1.25$ is critical for the $(VS)_x(Fe_2O_3)_{2-x}$ system, because it is at this concentration that the conductivity crosses over from the semiconducting to semimetallic type.

As the monosulfide concentration x in the vanadium oxysulfide system increases, the drop in ρ within the range 77–300 K increases from 1.5 orders of magnitude for $x = 0.9$ to nine orders for $x = 1.25$.

The oxysulfide with $x = 1.25$ in the range 150–180 K undergoes a change in the conductivity type from the semiconductor to the semimetal with a change in the electrical resistivity from 10^8 to 10^{-1} Ωcm.

3.4. Magnetic properties. Figure 2 shows temperature dependences of the real component of the initial magnetic susceptibility for the $(VS)_x(Fe_2O_3)_{2-x}$ system with compositions $x = 0.9$ and 1.1. The composition with $x = 0.9$ was found to have an anomaly in the $\chi'(T)$
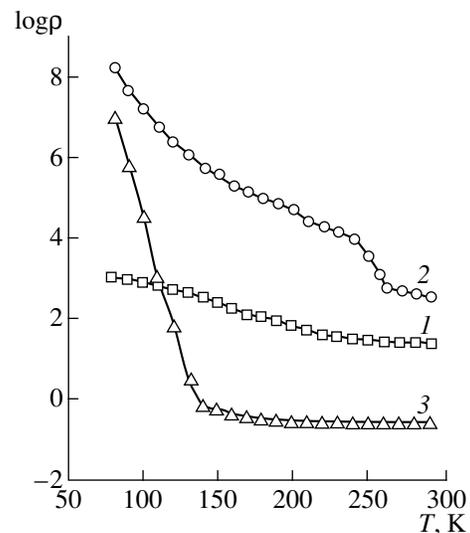
Fig. 1. Temperature dependences of the electrical resistivity of the $(VS)_x(Fe_2O_3)_{2-x}$ system: $x = (1)$ 0.9, (2) 1.1, and (3) 1.25.
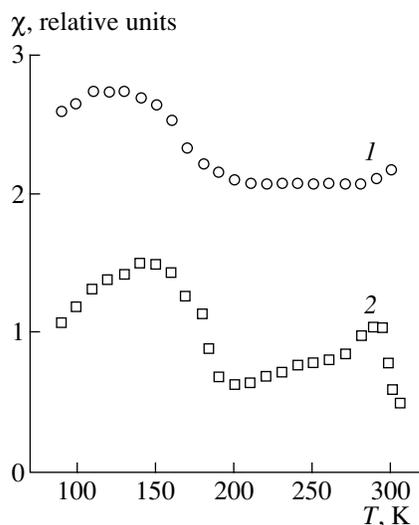
Fig. 2. Temperature dependences of the magnetic susceptibility of the $(VS)_x(Fe_2O_3)_{2-x}$ system. x: (*1*) 0.9 and (*2*) 1.1.

Fig. 3. Temperature dependence of the magnetic susceptibility of the $(VS)_{1.25}(Fe_2O_3)_{0.75}$ composition.
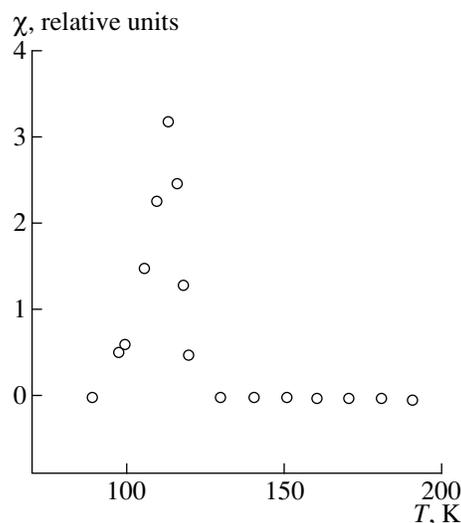
curve in the range 80–210, which peaks at 125 K. In the range 210–280 K, the $\chi'(T)$ curve is temperature independent, with subsequent increase in the susceptibility as one approaches 300 K. The composition with $x = 1.1$ exhibits two broad peaks in the $\chi'(T)$ curve at 145 and 298 K.

Figure 3 displays the $\chi'(T)$ curve for the composition with $x = 1.25$. As is seen from the temperature dependence of the magnetic susceptibility, this composition reveals the magnetization within a limited temperature range from 90 to 120 K with a peak at 115 K and two magnetic transformation points at 90 and 120 K.

The present experimental studies of the physical properties of the $(VS)_x(Fe_2O_3)_{2-x}$ oxysulfide system with compositions in the range $0.9 < x < 1.25$ allow the following conclusions on the correlation between the electrical and magnetic characteristics.

(1) As the sulfide concentration x in samples of the system increases, one has observed (i) a concentration-driven semiconductor–semimetal transition at $x_c = 1.25$; and (ii) an anomaly in the magnetic susceptibility in the range 80–210 K for compositions with $x = 0.9$ and 1.1, followed by an increase in the susceptibility, which is replaced by the onset of magnetization within the limited temperature range 90–120 K for $x = 1.25$.

(2) Measurements of the temperature behavior of the electrical resistivity and susceptibility showed that (i) for the composition with $x = 0.9$, a monotonic change in the conductivity type at $T > 240$ K is accompanied by a change in the $\chi'(T)$ curve from a temperature-dependent to temperature-independent character in the range $210 < T < 290$ K; and (ii) for the composition with $x = 1.1$, similar to $x = 1.0$ [3], the change in ρ

by an order of magnitude at 240–300 K is accompanied by the appearance of a peak in the $\chi'(T)$ curve at 298 K.

(3) The results obtained for the composition with $x = 1.25$ appear interesting. The semiconductor–semimetal crossover in the conductivity type entailing a change in ρ by nine orders of magnitude in the range 160–180 K is accompanied by structural changes and a symmetry lowering. One has also observed the existence of magnetization at 90–120 K with a peak at 115 K in the $\chi'(T)$ curve and two magnetic-transition points.

4. DISCUSSION

The electronic structure of the $FeS \cdot Fe_2O_3$ oxysulfides has recently been discussed [3] in terms of the band structure of the Fe_3O_4 magnetite. Both compounds are characterized by ferrimagnetic ordering of the iron ions. Below the Verwey point, the formula of the iron oxysulfide can be presented in the form $Fe_A^{3+}S^{2-}Fe_B^{2+}Fe_B^{3+}O_3^{2-}$. The current carriers are the t_{2g} electrons in the B sublattice moving in a narrow d band characterized by strong electron correlations. Based on the data obtained for $FeS \cdot Fe_2O_3$, and assuming the spinel lattice is retained, one can propose the formula $V_A^{3+}S^{2-}Fe_B^{2+}Fe_B^{3+}O_3^{2-}$ for the $VS \cdot Fe_2O_3$ compound. The V^{3+} ion occupying a tetrahedral site has two d electrons in the e_g orbitals; the e_g band formed by these electrons is half-filled and also experiences the effects of strong electron correlations. The correlations make the vanadium e_g band split into a lower and upper Hubbard subbands with the Fermi level falling in the Mott–Hubbard gap for $x = 1$. In compositions with $x = 1$, the e_g band is filled less than one half for $x < 1$, and above one half for

$x > 1$. Electron transfer from the vanadium to iron bands, and electron collectivization to form narrow d bands, complicates the pattern of the electronic structure. Nonetheless, there is no question that the carriers in the compounds under study are strongly correlated electrons from the narrow d bands, for which transitions between localized and delocalized states induced by slight variations of external parameters (temperature, composition, etc.) are typical [4]. One can thus visualize various modes of behavior, which should affect both the electrical and magnetic properties.

Because V^{3+} has $S = 1$, the $(VS)_x(Fe_2O_3)_{2-x}$ system should be ferrimagnetic. A comparison of curves 1 and 2 in Figs. 1 and 2 shows that, in the region of semimetallic conductivity, the susceptibility follows the Pauli-type temperature dependence, which implies that the d electrons are delocalized. As the temperature decreases to the level where the conductivity is activated, the temperature dependence of the susceptibility takes on the form characteristic of localized electrons. Thus, the changes in the temperature behavior of the electrical and magnetic properties for compositions with $x = 0.9$ and 1.1 are correlated.

For the composition with $x = 1.25$, the situation is more complex. Here, the ferromagnetic region existing in a narrow temperature range appears below $T = 160$ K, where the conductivity crosses over from the semimetallic to semiconducting character. Magnetic phases of this type were predicted in [1] as the result of the temperature-induced exchange in the system of band carriers, whose concentration in the semiconducting phase increases with a rise in the temperature. Another possible reason may be that the ferron states becoming stabilized [5] inside the two-sublattice matrix, ferrimagnetic in our case. A similar temperature dependence of the magnetization with a narrow peak near 473–533 K is known to occur in the FeS_x iron sulfide system with $x = 1.11$ [6, 7].

ACKNOWLEDGMENTS

REFERENCES

1. A. A. Berdyshev, *Exchange Interactions in Magnetically Ordered Solids and the Associated Effects*, Doctoral Dissertation in Mathematical Physics (Sverdlovsk, 1975).
2. L. R. Bickford, Rev. Mod. Phys. **25**, 75 (1953).
3. G. V. Loseva, G. M. Mukoed, S. G. Ovchinnikov, *et al.*, Fiz. Tverd. Tela (Leningrad) **34**, 1765 (1992) [Sov. Phys. Solid State **34**, 940 (1992)].
4. N. F. Mott, *The Metal–Insulator Transitions* (Taylor & Francis, London, 1974; Nauka, Moscow, 1979).
5. É. L. Nagaev, *Physics of Magnetic Semiconductors* (Nauka, Moscow, 1979).
6. T. Hihara, J. Sci. Hirosima Univ., Ser. A **24**, 31 (1960).
7. G. V. Loseva, S. G. Ovchinnikov, and G. A. Petrakovskiǐ, *The Metal–Dielectric Transition in 3d Metal Sulfides* (Nauka, Novosibirsk, 1983).

Translated by G. Skrebtsov