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MAGNETISM AND FERROELECTRICITY

Transition from the Kondo Regime to Long-Range Magnetic Order in the $Fe_xV_{1-x}S$ System

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Abstract—A study is reported on the electrical and magnetic characteristics of the $Fe_xV_{1-x}S$ solid-solution system with $x \le 0.5$. A maximum in the temperature dependence of resistivity $\rho(T)$ characteristic of the Kondo effect has been observed for small x ($x < 0.01$). For $x > 0.1$, long-range magnetic order sets in in the system with $T_K \sim 100$ K. Near $x = 0.05$, the Fe^{2+} impurity behavior crosses over to a magnetically ordered phase. The electronic properties of $Fe_xV_{1-x}S$ are typical of those of strongly correlated electronic systems. Both the electrical and magnetic data imply that carrier delocalization is the strongest at $x = 0.4$. © *2000 MAIK "Nauka/Interperiodica".*

Many vanadium compounds differing in crystalline structure, such as oxide spinels $Li_xMe_{1-x}V_2O_4$ (Me stands for Zn and Mg) [1], perovskites $Sr_xLa_{1-x}TiO_3$ [2], and NiAs-type sulfides with a superstructure, such as $Me_xV_{1-x}S$ (with Me standing for a 3*d* metal) [3, 4], undergo a metal–insulator transition and are studied intensely to understand specific features of the electronic and magnetic states in strongly correlated electronic systems. Spin fluctuations play a prominent part in such electronic systems.

This paper reports a temperature study of the electrical resistivity ρ and magnetization σ of the $Fe_xV_{1-x}S$ system with compositions $0 < x \le 0.5$ in the 4.2–300 K temperature range. The concentration dependences of ρ and σ for compositions with $0.1 \le x \le 0.5$ are presented in [3].

1. EXPERIMENTAL TECHNIQUES

The preparation technology of polycrystalline $Fe_xV_{1-x}S$ samples, which is the same for all compositions studied, is described in [3].

The resistivity was measured by the four-probe dc potentiometric method. The samples intended for resistivity measurements were pressed to $10 \times 5 \times 2$-mm parallelepipeds and fired in evacuated quartz ampoules at 1200 K for an hour.

The magnetization was measured in an automated vibrating-sample magnetometer with a superconducting coil in magnetic fields of up to 0.1 T.

Temperature measurements of the real part of the initial magnetic susceptibility χ' were carried out on a setup including an inductance bridge and a phase-sensitive detector.

The magnetic and resistivity measurements were done on the same samples.

2. EXPERIMENTAL RESULTS

2.1. X-ray Diffraction Characterization and DTA

X-ray diffraction studies of $Fe_xV_{1-x}S$ compounds with isomorphous substitution of Fe for V were performed at $T = 300$ K and showed them to be isostructural with V_5S_8 (monoclinic superstructure $F2/m$–C^3) for $0.1 \le x \le 0.5$ [3]. The compositions with low iron concentrations $x = 0.005$, 0.01, 0.02, and 0.05 had a distorted superstructure close to that of V_5S_8. All the compositions studied revealed in DTA curves two reversible endothermic effects at 800–900 K falling into the metal–insulator transition region of the starting monosulfide VS [3]. In the present work, the DTA range was extended to 1300 K, which allowed the determination a peak at 1020–1100 K in DTA curves obtained on $0.1 \le x \le 0.5$ compositions. The peak corresponded to the Curie temperature θ_C, and its observation provided an indirect method for measuring this temperature.

2.2. Electrical Resistivity

The concentration dependence of the electrical resistivity obtained at 80 and 300 K exhibits a strong increase of ρ to 0.6 Ω cm for $x = 0.1$ at room temperature, with its subsequent drop by an order of magnitude with increasing iron concentration, which evidences the electron localization to be the strongest at $x = 0.1$. Figure 1 presents $\rho(T)$ curves for compositions with low iron concentrations. As is seen from Fig. 1a, the $\rho(T)$ dependence obtained for the $x = 0.005$ composition (0.25 at. % Fe) passes through a maximum at $T \sim 90$ K. Such $\rho(T)$ behavior was observed for dilute metal

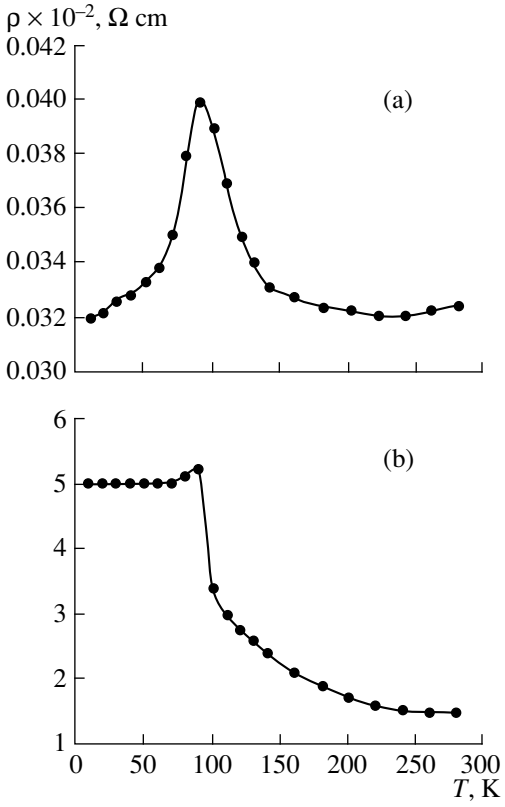

Fig. 1. Temperature dependences of the electrical resistivity of $Fe_xV_{1-x}S$ samples for compositions with (a) $x = 0.005$ and (b) $x = 0.05$.

alloys with low concentrations of paramagnetic impurities in the lattice in the absence of magnetic order, i.e., the Kondo effect [5]. The amplitude of the peak in $\rho(T)$ was found to depend on the paramagnetic impurity concentration and external magnetic field and to become suppressed as the latter increase.

As the iron concentration increases to $x = 0.05$, the general resistivity increase by more than two orders of magnitude is accompanied by the disappearance of the $\rho(T)$ peak, although traces of the temperature anomaly can still be detected around 90 K (Fig. 1b). For $T > 90$ K, the $\rho(T)$ curves follow a close-to-activated behavior for both compositions.

The influence of a further increase of the iron concentration can be seen from Fig. 2, which shows that the $\rho(T)$ dependence levels off with increasing x, to approach a semimetallic conduction pattern at $x = 0.4$ throughout the temperature range studied.

2.3. Magnetic Properties

Measurements of the low-frequency magnetic susceptibility $\chi'(T)$ did not reveal long-range magnetic order in samples with iron concentration $x < 0.1$.

As for compositions with higher iron contents, the saturation field, as seen from the magnetization curves displayed in Fig. 3, is approximately the same for all samples with $x \geq 0.1$, with the magnetization varying noticeably in magnitude. It is apparently the high values of θ_C that account for the fact that the values of $\sigma(H)$ measured at 68 and 300 K differ by not more than 5%. The fact that the magnetization curves reach saturation at magnetic fields of about 0.1 T, as well as the high values of the magnetization, suggests that the exchange interaction has a ferromagnetic component, which is buttressed by the observation of hysteresis loops with a coercive force $H_C \sim (3–5) \times 10^{-4}$T.

The magnetic moments M per iron atom derived from the magnetization curves are displayed in Fig. 4, and Fig. 5 presents the values of θ_C obtained for various compositions. We note with interest a correlation between these two dependences within the concentration range studied.

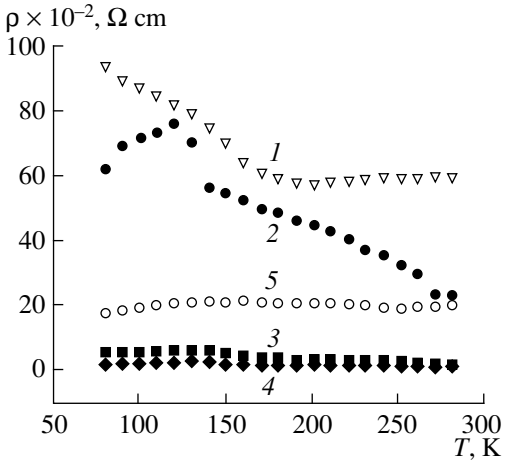

Fig. 2. Temperature dependences of the electrical resistivity of $Fe_xV_{1-x}S$ samples for compositions with x: (*1*) 0.1, (*2*) 0.2, (*3*) 0.3, (*4*) 0.4, and (*5*) 0.5.

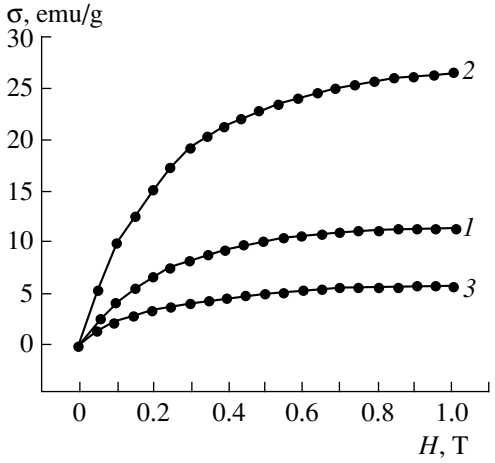

Fig. 3. Magnetization curves of $Fe_xV_{1-x}S$ samples for x: (*1*) 0.1, (*2*) 0.2, and (*3*) 0.4.

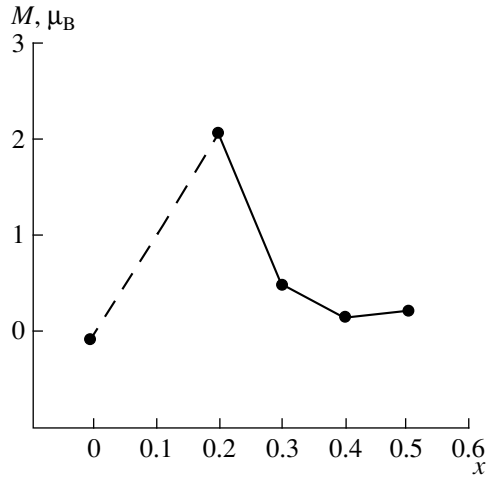

Fig. 4. Concentration dependences of the magnetic moment M per Fe atom.

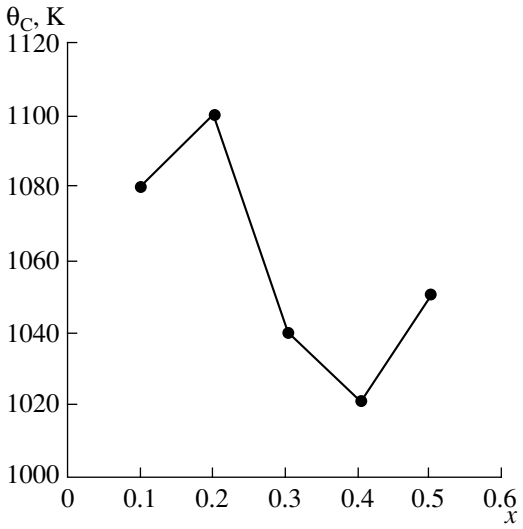

Fig. 5. Concentration dependences of the Curie temperature θ_C.

3. DISCUSSION OF RESULTS

As follows from the x-ray diffraction data, $Fe_xV_{1-x}S$ and V_5S_8 with ordered vacancy layers have similar structures and the substitutional Fe atoms are ordered in hexagonal layers. An analysis of the electronic structure [3] showed that, at low concentrations, each iron atom forms a localized magnetic impurity with $S = 1$. It is carrier scattering from such impurities that produces, as is well known, the Kondo effect, and therefore, its manifestation in $\rho(T)$ curves with $x = 0.005$ does not appear strange. For $x \geq 0.1$ there is long-range magnetic order, where the Kondo effect is suppressed. The crossover between the Kondo regime and long-range magnetic order occurs at an impurity concentration x_C such that $T_K \sim x_C\theta_C$ [5], where T_K is the Kondo temperature and θ_C is the Curie temperature of a concentrated magnetic system. In our case, $T_K \sim 100$ K and $\theta_C \sim 1000$ K, so that $x_C \sim 0.1$. Indeed, for $x = 0.05$, as seen from Fig. 1b, $\rho(T)$ follows an intermediate behavior with a pronounced spin fluctuation contribution for $T > 100$ K, i.e., this composition apparently lies near the crossover from one regime to the other.

At $x \sim 0.1$–0.2, the magnetically ordered phase is characterized by magnetic moments localized on Fe atoms which evidences strong *d*-electron correlations in Fe. As x increases still further, the wave-function overlap of the *d* electrons becomes enhanced to give rise to their partial delocalization, which is seen from the sharp drop of the magnetic moment of Fe atoms and the leveling off of the temperature dependence $\rho(T)$. Judging from both electrical and magnetic measurements, the delocalization is strongest near $x = 0.4$.

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