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Influence of solubility of MoO_3 in $SbVO_5$ on the magnetic spin arrangement

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ABSTRACT

The magnetic properties of the solid solutions of MoO_3 in $SbVO_5$ for 5, 10 and 15 mol% were investigated by the magnetic susceptibility $\chi_\sigma(T)$ and magnetization $\sigma(B)$. With increasing MoO_3 in $SbVO_5$ from 5 to 10 mol% the antiferromagnetic order shifts to higher temperatures and a Néel temperature of $T_N \approx 6$ K accompanied with a negative increase of the Curie–Weiss temperature from $\theta_{CW} \approx -6$ K to -58 K is observed, indicating a change in the magnetic structure from non-collinear of the Yafet–Kittel type to a collinear antiferromagnetism. For 15 mol% a conical magnetic spin arrangement is likely. The values of the electrical resistivity $\rho(T)$ and of the thermopower S at high temperatures indicate that all solid solutions are thermally activated p-type semiconductors above 325 K.

1. Introduction and experimental

The oxides V_2O_5, MoO_3, α-Sb_2O_4 and their compounds occurring in the two and three component systems are active and selective basic components of catalysts in the modern chemical processes and petroleum refining [1–3]. A study of theoretically possible vacancy models [4] showed that Mo^{6+} ions were incorporated in the $SbVO_5$ monoclinic structure [4] instead of Sb^{5+} and/or V^{5+} ions and the compensation of the redundant positive charges took place through cation vacancies arising in the Sb^{5+} and/or V^{5+} sub-lattice. For each sample a vacancy model was introduced and the molybdenum, antimony and vanadium contents were recounted and expressed by the vacancy parameter x in the chemical formula (Table 1).

Monophase samples of the mixed oxide solid solutions MoO_3 in $SbVO_5$ have been prepared by solid-state reaction in air at temperatures not exceeding 918 K [4]. The molybdenum, antimony and vanadium contents were quantitatively determined for some selected samples using scanning electron microscope (JSM-1600, JEOL, Japan) linked to an X-ray microanalyser (ISIS 300, Oxford). Analysis of the chemical composition of the surface of selected monophase preparations was made by X-ray Photoelectron Spectroscopy (XPS) with an apparatus designed by the company Vacuum Systems Workshop Ltd., England equipped with an 18-channel, two-plate detector (Galileo) and working voltage–1.8 kV. Pressure in the analytical chamber was 2×10^{-8} mbar. The data were acquired using Al $K\alpha_{1,2}$ radiation (1486.6 eV, 210 W). The phase analysis for the solid solutions under study was made by the X-ray DRON-3 diffractometer using Co Kα radiation with the Fe filter. The parameters of selected unit cell were refined using the REFINEMENT program of the DHN/PDS package [4].

The mass susceptibility, magnetization, electrical resistivity and thermopower measurements were carried out on the solid solutions with 5, 10 and 15 mol% content of MoO_3 in $SbVO_5$ using a: (1) Cahn automatic magnetic electrobalance of the Faraday type in the temperature range 3.9–400 K and in applied external field H = 1.5 kOe. A correction for diamagnetic contribution has been taken into account [5] and the Curie–Weiss law was fitted by adding a temperature independent residual susceptibility χ_0 (Table 2), (2) step-magnetometer at 4.2 K and in applied external fields up to 14 T, (3) 4-point dc method for $\rho(T)$ in the temperature range 300–500 K using a semi-automatic bridge [6] containing

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Table 1
Chemical formulas and vacancy model for solid solutions of MoO_3 in $SbVO_5$.

x	MoO_3 (mol%)	Chemical formula	Vacancy model
0.0051	5.00	$Sb_{1-6x}\square_x V_{1-6x}\square_x Mo_{10x}O_5$ ($\Sigma\square = 0.0102$)	The Mo^{6+} ions are incorporated into $SbVO_5$ in equal number for V^{5+} and Sb^{5+} ions, and a compensation of excessive charges is accomplished through vacancies (□) at the V^{5+} and Sb^{5+} sites in 1:1 proportion
0.0104	10.00	$Sb_{1-6x}\square_x V_{1-6x}\square_x Mo_{10x}O_5$ ($\Sigma\square = 0.0208$)	
0.0159	15.00	$Sb_{1-6x}\square_x V_{1-6x}\square_x Mo_{10x}O_5$ ($\Sigma\square = 0.0318$)	

$\Sigma\square$ means a content of vacancies in a molecule.

Table 2
Magnetic and electrical parameters for solid solutions of MoO_3 in $SbVO_5$.

MoO_3 (mol%)	μ_{eff} (μ_B/f.u.)	μ (μ_B/f.u.)	T_N (K)	θ_{CW} (K)	χ_0 (cm^3/g)	E_A (eV)	S (μV/K)
5	0.67	0.0047	5.7	−6.3	2.822×10^{-6}	0.877	117
10	1.07	0.0029	6	−58	3.093×10^{-6}	0.644	18
15	0.58	0.0054	4; $T_C = 250$	241	1.237×10^{-6}	0.649	50

μ_{eff} is the effective magnetic moment, μ is the magnetic moment at 4.2 K and at 14 T, T_N, T_C and θ_{CW} are the Néel, Curie and Curie–Weiss temperatures, respectively, χ_0 is the temperature independent residual susceptibility, E_A is the activation energy at 400 K and S is the thermopower at 450 K.

the CA3160 integral circuit with the input impedance of 1.5 TΩ and the HP 34401A digital multimeters controlled by the computer and LabView® commands. The maximal error $\delta\rho/\rho$ was less than ±1%. The activation energy E_A was determined from the formula: $\rho^{-1} = \rho_0^{-1}\exp(-E_A/k_BT)$, where k_B is the Boltzmann's constant, and (4) differential method [7] with the temperature gradient $\Delta T \approx 5$ K for S at 450 K. The accuracy of the value of thermopower was estimated to be better than 3 μV/K. For electrical measurements the powder samples were compacted in disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and they were next sintered through 2 h at 873 K.

2. Results and discussion

Fig. 1 shows the temperature dependence of the mass susceptibility $\chi_\sigma(T)$ vs. T (left axis) and $1/\chi_\sigma(T)$ (right axis) for the three solid solutions 5, 10 and 15 mol% in the temperature range $3.9 < T < 400$ K in a magnetic field of $B = 0.15$ T. The solid lines represent a Curie–Weiss fit to the data at high temperatures with the calculated parameters in Table 2, respectively. For 10 mol% T_N increases and a kink at $T_N = 6$ K is observed, furthermore the negative value of the Curie–Weiss temperature increases from $\theta_{CW} = -6.3$ K to $\theta_{CW} = -58$ K compared to sample with 5 mol%. For

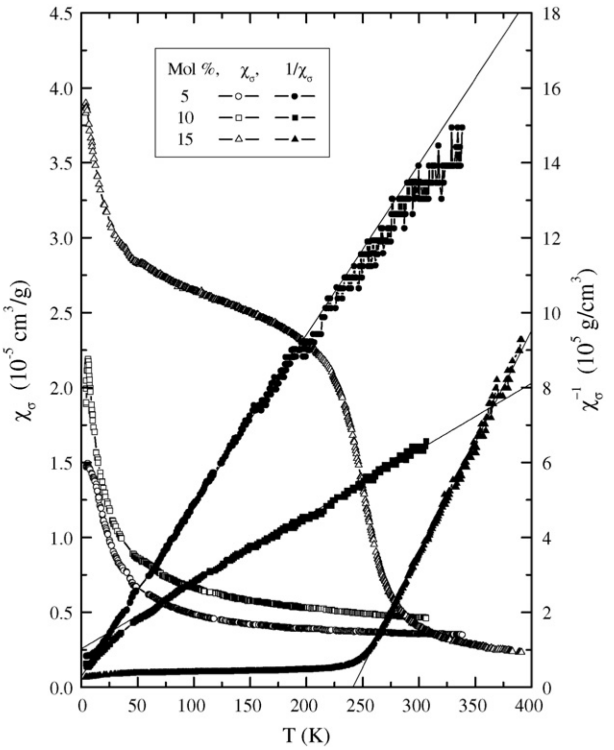

Fig. 1. Mass susceptibility χ_σ and $1/\chi_\sigma$ vs. temperature T for samples with 5, 10 and 15 mol% of MoO_3 in $SbVO_5$ with $B = 0.15$ T.

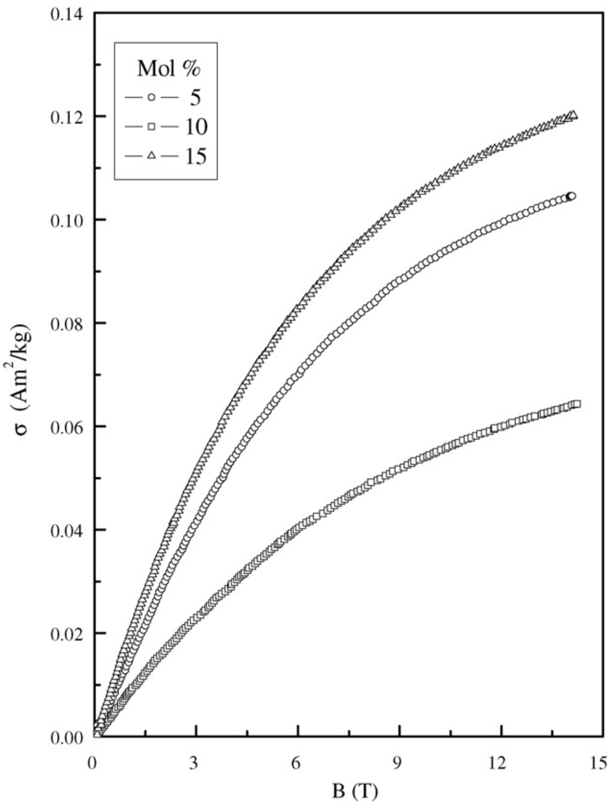

Fig. 2. Magnetization σ vs. magnetic induction B at 4.2 K for samples with 5, 10 and 15 mol% MoO_3 in $SbVO_5$.

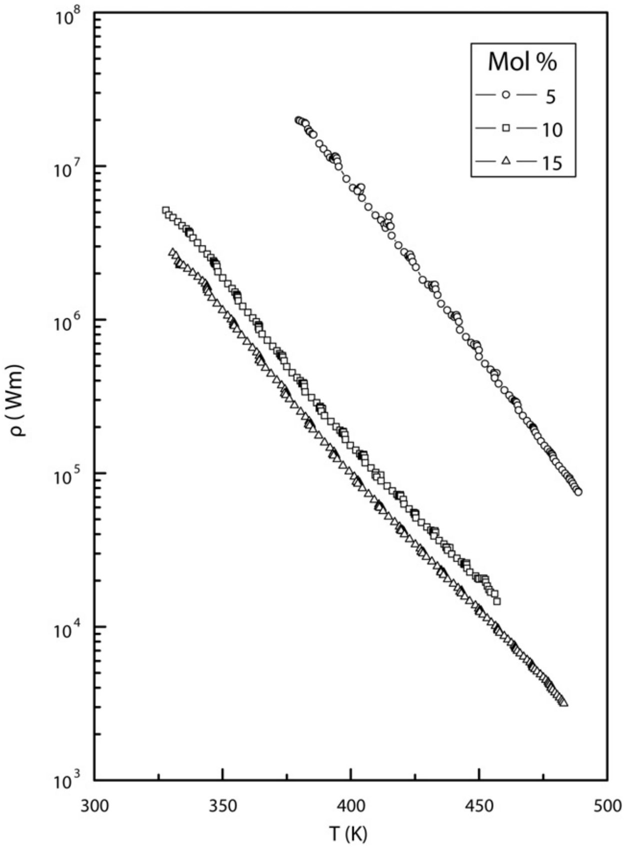

Fig. 3. Electrical resistivity ρ vs. temperature T for samples with 5, 10 and 15 mol% of MoO_3 in $SbVO_5$.

the solid solution with 15 mol% the $\chi_\sigma(T)$ data shows a broad ferromagnetic transition at $T_C = 250$ K and below at $T_N = 4$ K a further increase, possible indication for a second magnetic transition. Additionally the magnetization σ (Fig. 2) at $T = 4.2$ K was measured on the three samples up to $B = 14$ T. A nonlinear increase of the magnetization with increasing field is observed for all samples and a small value of $\sigma \approx 0.12$ emu/g for 15 mol% is found at $B = 14$ T. This means that a weak spontaneous magnetization exists in the sample. At first sight the magnetic results of $\chi_\sigma(T)$, $1/\chi_\sigma(T)$ and $\sigma(B)$ presented above seem to be very strange because in the solid solutions under study all ions are nonmagnetic and simultaneously the parasitic magnetism exists. However, occurrence of the parasitic magnetism well correlates with the XPS spectra [4]. They have shown that the vanadium, antimony and molybdenum occurred mainly as V^{5+}, Sb^{5+} and Mo^{6+} in the bulk of the solid solutions under study while their surfaces contained very small amounts of Sb^{3+} and Mo^{4+} ions. Probable the Sb^{5+} and Mo^{6+} ions might be partially reduced to Sb^{3+} and Mo^{4+} ions, respectively, on the surfaces of samples enriched in Sb and Mo. From these two reduced ions only the Mo^{4+} ions in the high spin configuration can bear a magnetic moment.

The values of $\rho(T)$ (Fig. 3) in the temperature range 300–500 K and the positive thermopower S at $T = 450$ K reveal that the solid solutions under study are insulators and reveal a week p-type conductivity above 325 K. The linear dependence of $\rho(T)$ decreases with increasing solubility of MoO_3 in $SbVO_5$ accompanied with the cation vacancies (Table 1), suggesting that the nature of hole conductivity may originate from the cation Sb^{5+} and V^{5+} vacancies forming the vacancy acceptor narrow bands. However, the relatively high values of the activation energy E_A (Table 2) comply with the intrinsic type of conductivity rather than extrinsic conduction. Thus, the charge transport may occur through the thermal-activated hopping of 3d electrons via cation vacancies. Similar mechanism of conductivity has been observed in the n-type antiferromagnetic $Fe_2V_{4-x}Mo_xO_{13}$ [8], $FeVO_4$, $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$ oxides [9] as well as in the iron-tungsten-oxygen system Fe_2WO_6 [10].

One can conclude that with increasing molar solubility of MoO_3 in $SbVO_5$ both a vacancy parameter and a total vacancy concentration increase leading to an occurrence of a parasitic magnetism. Its magnetic spin arrangement is changed from a non-collinear antiferromagnetism of the Yafet–Kittel type [11] with a low both Curie–Weiss temperature $\theta_{CW} = -6.3$ K and Néel temperature $T_N \approx 5.7$ K in the solid solution 5 mol% to collinear antiferromagnetism with a large negative Curie–Weiss temperature $\theta_{CW} = -58$ K, low Néel temperature $T_N \approx 6$ K and high $\mu_{eff} = 1.07\ \mu_B$ at 10 mol%. In 15 mol% a large positive Curie–Weiss temperature $\theta_{CW} = 241$ K suggests that a ferromagnetic phase is present in a sample, too, involving a large Curie temperature $T_C = 250$ K, finally forming a conical magnetic structure. This may result from a weakness of the antiferromagnetic coupling by the larger number of the non-magnetic cation vacancies ($\Sigma\square = 0.0318$) causing also a decrease of the temperature independent residual susceptibility χ_0 at 15 mol% (Table 2). It is worth to notice that the χ_σ value is larger only about one order of magnitude than χ_0 one indicating the significant Pauli or Van Vleck contributions to the total susceptibility (see Fig. 1 and Table 2).

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