

# Crystal Structure and Magnetic Properties of Pyrrhotite-Type Compounds $\text{Fe}_{7-y}\text{V}_y\text{S}_8$

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The pyrrhotite-type compounds  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  have been synthesized and studied by means of the X-ray diffraction and magnetization measurements in order to reveal how the substitution of V for Fe affects the crystal structure, phase transition and magnetic properties. The growth of the V content in  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  results in changes of the crystal structure and leads to a sharp decrease in the resultant magnetization, non-monotonous change of the coercive field and reduction of the magnetic ordering temperature. Unlike ferrimagnetic ordering in pyrrhotite  $\text{Fe}_7\text{S}_8$  the compound  $\text{V}_7\text{S}_8$  is observed to exhibit a Pauli-paramagnetic behaviour.

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## 1. Introduction

Pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) consists of completely filled layers of chalcogen sandwiched between Fe layers one of which is full, while another one contains vacancies [1]. The Fe magnetic moments ( $\mu_{\text{Fe}} \sim 3.2\mu_{\text{B}}$ ) are arranged parallel to each other inside each layer, but are coupled antiparallel to each other between successive layers [2]. The presence of vacancies in every second Fe layer leads to incomplete compensation of magnetic moments and to a ferrimagnetic order which enters below the Neel temperature of about 590 K [1,2]. The magnetic properties of  $\text{Fe}_7\text{X}_8$  are strongly influenced by substitutions in both the Fe [3, 4] and chalcogen sublattices [5]. The replacement of iron in  $\text{Fe}_{7-y}\text{M}_y\text{X}_8$  ( $\text{X} = \text{S}, \text{Se}$ ) by other 3d metal ( $\text{M} = \text{Ti}, \text{Co}$ ) atoms in cation layers is found to be non-random and dramatically affects the magnetic behavior [4]. The cation partitioning between layers in pyrrhotite-type compounds is observed to depend on the kind of substituting M atoms assumingly owing to the difference in the spatial extension of 3d orbitals [4]. In order to confirm this suggestion further the present work aims to study how the substitution of V for Fe affects the properties of the  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  compounds.

## 2. Experimental

Polycrystalline samples  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  ( $y = 0-7$ ) were obtained by solid-state reactions in evacuated quartz tubes. The starting materials were small vanadium pieces (99.9% purity), sulfur (99.99%) and powder of iron (99.98%). The method of synthesis of  $\text{Fe}_{7-y}\text{M}_y\text{S}_8$  samples has already been described in detail [4]. In order to examine the quality of the samples and the changes in the crystal structure upon substitution a powder X-ray

diffractometer Bruker D8 ADVANCE with Cu  $K\alpha$  radiation was used. The measurements of the magnetic susceptibility and magnetization were performed by means of a Quantum Design SQUID MPMS magnetometer and Vibrating sample magnetometer Lake Shore VSM 7407.

## 3. Results

According to X-ray diffraction all the synthesized samples  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  ( $0 \leq y \leq 7$ ) have layered superstructures of the NiAs-type, while in the case of Ti for Fe substitution, the single phase  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$  samples were obtained only at  $y \leq 4$  [3]. The changes in the crystal structure in  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  with substitution can be characterized by the lattice parameters  $a_0$  and  $c_0$  of the NiAs fundamental unit cell. The V for Fe substitution is found to result in the growth of the  $c_0$  value from 5.668(6) Å in  $\text{Fe}_7\text{S}_8$  ( $y = 0$ ) up to 5.789(2) Å in  $\text{V}_7\text{S}_8$  ( $y = 7$ ), however, the average intra-layer distance characterized by lattice parameter  $a_0$  slightly decreases with increasing V content from 3.436(1) Å for  $y = 0$  down to 3.376(3) Å for  $y = 7$ .

The unit cell volume remains almost unchanged upon substitution in the  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  system.

The replacement of Fe by V atoms is observed to dramatically affect the magnetization behaviour in magnetic fields (shown in Fig. 1). As in the case of the Ti for Fe substitution [3, 4], the replacement of Fe by V up to  $y = 1$  significantly reduces the magnetization, while further growth of the V content results in a non-monotonous change of the magnetization. Fig. 2a shows the concentration dependence of the magnetization  $M_{50}$  measured in a field of 50 kOe at temperature 2 K on the  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  samples. The non-monotonous behaviour of the magnetization was also observed in the  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$  system, which was explained by the ferrimagnetic ordering of the Fe magnetic moments and by non-random substitutions in the cation layers [3, 4] since the statistical distribution of substituting atoms should result in the monotonous reduction of the resultant magnetization.

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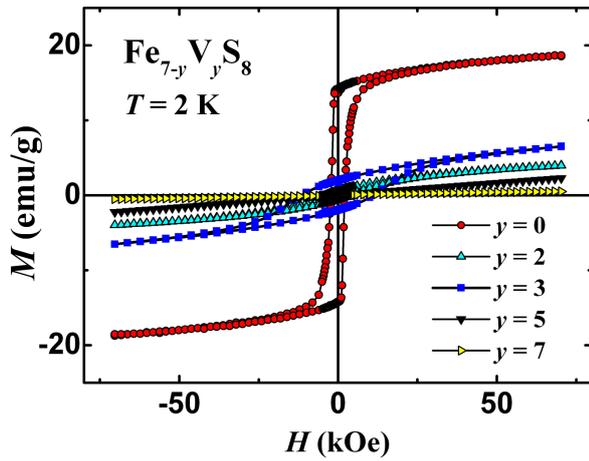


Fig. 1. Field dependences of the magnetization measured at  $T = 2$  K on the  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  samples.

For  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ , the non-random Ti for Fe substitution in alternating cationic layers was derived from neutron diffraction data [4]. The presence of a minimum of the resultant magnetization at  $y \sim 1.5$  in  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  may be associated with the compensation of the sublattice magnetizations, as in  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$  [3, 4]. However, unlike the  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$  samples with  $y > 1.5$  exhibiting almost in twice increased magnetization in high magnetic fields in comparison with the non-substituted  $\text{Fe}_7\text{S}_8$  compound, all the  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  compounds demonstrate substantially lower values of the resultant magnetization. There are several origins which may lead to reduced values of the magnetization in the V-substituted compounds: i) the less pronounced partitioning of Fe and V between adjacent layers; ii) the more random distribution of vacancies in all cationic layers and iii) presence of a non-zero magnetic moment on V ions unlike Ti. The neutron diffraction measurements are needed in order to reveal the main factors determining the magnetization behavior with increasing V content in  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ .

As follows from Fig. 2b, the substitution of V for Fe in  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  leads to the non-monotonous variations of the coercive field ( $H_c$ ), as in  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ . The growth of  $H_c$  around  $y = 1-1.5$  in both the V- and Ti-containing compounds apparently originates in the reduced values of magnetization. Such a behavior is analogous to that observed in vicinity of the compensation temperature in ferrimagnetic materials. When the V content increases up to  $y = 3$ , the hysteresis loop becomes broader and  $H_c$  reaches a value about of 11.5 kOe; further substitution of V for Fe reduces the hysteresis and leads to the paramagnetic behavior of  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  at  $y > 6$ .

The magnetic state of the V-substituted compounds  $\text{Fe}_{7-y}\text{V}_y\text{S}_8$  with  $y \sim 5$  seems to be non-homogeneous. The temperature dependence of the magnetic susceptibility of  $\text{Fe}_2\text{V}_5\text{S}_8$  (Fig. 3a) shows a remarkable hysteresis at low temperatures when the measurements were made on a sample cooled in zero field (ZFC) or on a sample cooled in an applied field (FC).

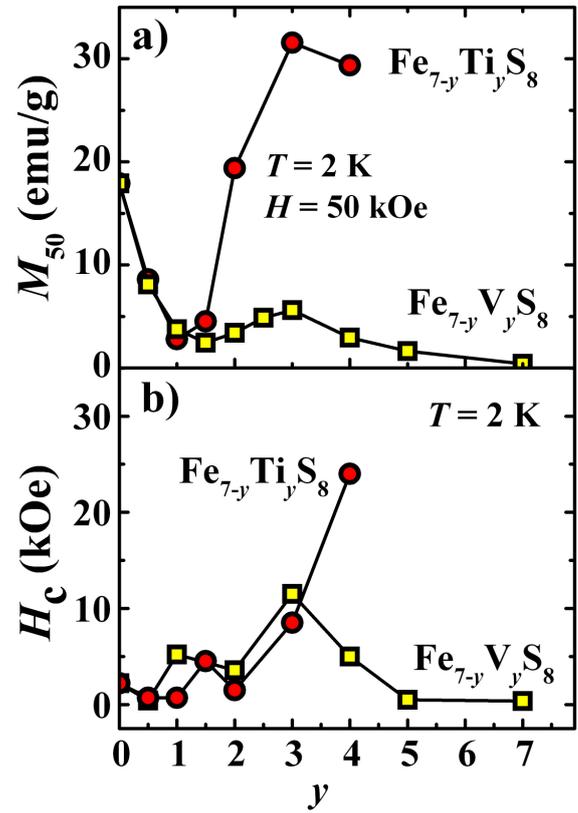


Fig. 2. Magnetization (a) in a field of 50 kOe and coercive field (b) for  $\text{Fe}_{7-y}\text{M}_y\text{S}_8$  ( $M = \text{V}, \text{Ti}$ ) at  $T = 2$  K as functions of the substituting atom concentrations. The data for  $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$  are taken from Ref. [4].

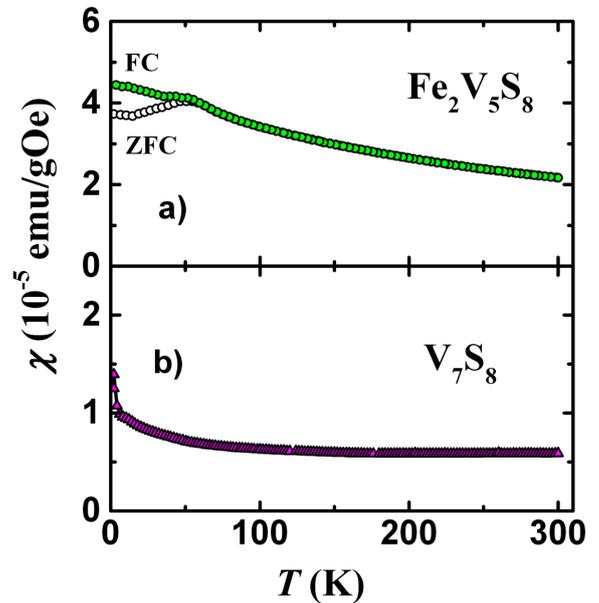


Fig. 3. Temperature dependences of the magnetic susceptibility for  $\text{Fe}_2\text{V}_5\text{S}_8$  (a) and  $\text{V}_7\text{S}_8$  (b) measured at  $H = 1$  kOe.

These data together with a reduced magnetization and broad hysteresis loop allow us to characterize the magnetic state of this compound as of cluster glass-type with freezing of the ferrimagnetic clusters below 50 K. As follows from Fig. 3b, the magnetic susceptibility of  $V_7S_8$  ( $y = 7$ ) shows weak temperature dependence above  $T \sim 100$  K and a low-temperature upturn of the Curie-Weiss (CW) type. Such a paramagnetic behavior of this compound is consistent with previously reported data for the vanadium sulfides with nearly equiatomic compositions [6]. The  $\chi(T)$  dependence for  $V_7S_8$  can be fitted to the expression:  $\chi(T) = \chi_0 + C/(T - \Theta_p)$ , in which the first term is the temperature-independent Pauli paramagnetic contribution from conduction electrons and the second one is the CW contribution from localized magnetic moments. From the Curie constant  $C$ , the effective magnetic moment  $\mu_{eff}$  was estimated to be  $0.3 \mu_B$  per V ion, which is substantially lower than the spin-only values for  $V^{3+}$  ( $2.83\mu_B$ ) and  $V^{4+}$  ( $1.73\mu_B$ ).

Figure 4 shows the variation of the magnetic ordering temperature ( $T_N$ ) with the V for Fe substitution in  $Fe_{7-y}V_yS_8$  together with the  $T_N(y)$  dependence for  $Fe_{7-y}Ti_yS_8$ . The Neel temperatures for the V-containing samples at  $y < 4$  are found to be greater than that for the compounds  $Fe_{7-y}Ti_yS_8$  with the same concentrations of the substituting elements.

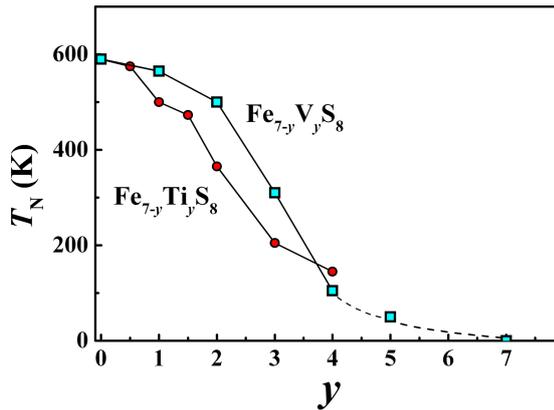


Fig. 4. The concentration dependences of the Neel temperature for  $Fe_{7-y}M_yS_8$  ( $M = V, Ti$ ). The data for  $Fe_{7-y}Ti_yS_8$  are taken from Ref. [4].

The enhancement of magnetic ordering temperatures in the  $Fe_{7-y}V_yS_8$  system may be indicative of the presence of a local magnetic moment on vanadium atoms in the compounds  $Fe_{7-y}V_yS_8$  with  $y < 4$  in contrast to the titanium atoms in  $Fe_{7-y}Ti_yS_8$ .

#### 4. Conclusions

The compounds  $Fe_{7-y}V_yS_8$  are found to exhibit the layered crystal structures of the NiAs-type in the whole concentration range. The growth of the V content increases the average inter-layer distance and reduces the average intra-layer distance, however, the unit cell volume remains almost unchanged upon substitution. The

replacement of Fe by V in  $Fe_{7-y}V_yS_8$  having a ferrimagnetic order at  $y = 0$  leads to a non-monotonous change of the resultant magnetization. A minimum of the magnetization around  $y = 1.5$  is attributed to the partial compensation of the antiferromagnetically ordered magnetic moments of 3d metal ions located in neighbor cationic layers because of non-random substitutions of V for Fe. The presence of such a minimum indicates that vanadium preferably substitutes iron in layers without vacancies when the V content increases up to  $y = 1.5$  as was observed earlier in the case of Ti for Fe substitution [4]. In  $Fe_{7-y}V_yS_8$ , the coercive field reaches a maximal value 11.5 kOe at  $y = 1.5$  obviously because of a reduced value of the resultant magnetization at this concentration. Unlike a non-monotonous variation of the resultant magnetization and coercive field the growth of the V content leads to a monotonous decrease of the magnetic ordering temperature. The  $Fe_{7-y}V_yS_8$  compounds are observed to exhibit a cluster-glass behavior within the concentration range  $4 < y \leq 6$ . A reduced value of the effective magnetic moment per V atom in  $V_7S_8$  ( $\mu_{eff} = 0.3 \mu_B$ ) indicates that the magnetic state of this compound can not be described in terms of a model with localized d electrons. The 3d electrons of V ions in the  $Fe_{7-y}V_yS_8$  system are rather in an intermediate regime between strongly localized and itinerant case.

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