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

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The pyrrhotite-type compounds Fe$_{7-y}$V$_y$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 Fe$_{7-y}$V$_y$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 Fe$_7$S$_8$ the compound V$_7$S$_8$ is observed to exhibit a Pauli-paramagnetic behaviour.

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1. Introduction

Pyrrhotite (Fe$_7$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 ($\mu_{Fe} \sim 3.2 \mu_B$) 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 Fe$_7$X$_8$ are strongly influenced by substitutions in both the Fe [3, 4] and chalcogen sublattices [5]. The replacement of iron in Fe$_{7-y}$M$_y$X$_8$ (X = S, Se) by other 3d metal (M = Ti, 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 Fe$_{7-y}$V$_y$S$_8$ compounds.

2. Experimental

Polycrystalline samples Fe$_{7-y}$V$_y$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 Fe$_{7-y}$M$_y$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 Kα 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 Fe$_{7-y}$V$_y$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 Fe$_{7-y}$Ti$_y$S$_8$ samples were obtained only at $y \leq 4$ [3]. The changes in the crystal structure in Fe$_{7-y}$V$_y$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 Fe$_7$S$_8$ ($y = 0$) up to 5.789(2) Å in V$_7$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 Fe$_{7-y}$V$_y$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 Fe$_{7-y}$V$_y$S$_8$ samples. The non-monotonous behaviour of the magnetization was also observed in the Fe$_{7-y}$Ti$_y$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 non-monotonous reduction of the resultant magnetization.

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For Fe$_{7-y}$Ti$_y$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 Fe$_{7-y}$V$_y$S$_8$ may be associated with the compensation of the sublattice magnetizations, as in Fe$_{7-y}$Ti$_y$S$_8$ [3, 4]. However, unlike the Fe$_{7-y}$Ti$_y$S$_8$ samples with $y > 1.5$ exhibiting almost in twice increased magnetization in high magnetic fields in comparison with the non-substituted Fe$_7$S$_8$ compound, all the Fe$_{7-y}$V$_y$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 Fe$_{7-y}$V$_y$S$_8$.

As follows from Fig. 2b, the substitution of V for Fe in Fe$_{7-y}$V$_y$S$_8$ leads to the non-monotonous variations of the coercive field ($H_c$), as in Fe$_{7-y}$Ti$_y$S$_8$. The growth of $H_c$ around $y \sim 1.5$ 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 Fe$_{7-y}$V$_y$S$_8$ at $y > 6$.

The magnetic state of the V-substituted compounds Fe$_{7-y}$V$_y$S$_8$ with $y \sim 5$ seems to be non-homogeneous. The temperature dependence of the magnetic susceptibility of Fe$_2$V$_5$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).
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 \( \text{V}_7\text{S}_8 \) \((y = 7)\) 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 \( \text{V}_7\text{S}_8 \) 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. Form the Curie constant \( C \), the effective magnetic moment \( \mu_{eff} \) was estimated to be 0.3 \( \mu_B \) per \( \text{V} \) ion, which is substantially lower than the spin-only values for \( \text{V}^{3+} \) \((2.83 \mu_B)\) and \( \text{V}^{4+} \) \((1.73 \mu_B)\).

Figure 4 shows the variation of the magnetic ordering temperature \( (T_N) \) with the \( \text{V} \) for \( \text{Fe} \) substitution in \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) together with the \( T_N(y) \) dependence for \( \text{Fe}_{7-y}\text{Ti}_y\text{S}_8 \). The Neel temperatures for the \( \text{V} \)-containing samples at \( y < 4 \) are found to be greater than that for the compounds \( \text{Fe}_{7-y}\text{Ti}_y\text{S}_8 \) with the same concentrations of the substituting elements.

![Fig. 4. The concentration dependences of the Neel temperature for \( \text{Fe}_{7-y}\text{M}_y\text{S}_8 \) \((M = \text{V}, \text{Ti})\). The data for \( \text{Fe}_{7-y}\text{Ti}_y\text{S}_8 \) are taken from Ref. [4].](image)

The enhancement of magnetic ordering temperatures in the \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) system may be indicative of the presence of a local magnetic moment on vanadium atoms in the compounds \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) with \( y < 4 \) in contrast to the titanium atoms in \( \text{Fe}_{7-y}\text{Ti}_y\text{S}_8 \).

4. Conclusions

The compounds \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) are found to exhibit the layered crystal structures of the NiAs-type in the whole concentration range. The growth of the \( \text{V} \) 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 \( \text{V} \) in \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) 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 \( \text{V} \) for Fe. The presence of such a minimum indicates that vanadium preferably substitutes iron in layers without vacancies when the \( \text{V} \) content increases up to \( y = 1.5 \) as was observed earlier in the case of Ti for Fe substitution [4]. In \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \), 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 \( \text{V} \) content leads to a monotonous decrease of the magnetic ordering temperature. The \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) compounds are observed to exhibit a cluster-glass behavior within the concentration range \( 4 < y < 6 \). A reduced value of the effective magnetic moment per \( \text{V} \) atom in \( \text{V}_7\text{S}_8 \) \((\mu_{eff} = 0.3 \mu_B)\) 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 \( \text{V} \) ions in the \( \text{Fe}_{7-y}\text{V}_y\text{S}_8 \) system are rather in an intermediate regime between strongly localized and itinerant case.

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