



Magnetic properties of a new vanadate $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$



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ABSTRACT

A new double vanadate, $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$, obtained by standard solid-state reaction method, has been studied by magnetic susceptibility and electron paramagnetic resonance (EPR) techniques. Measurements of dc susceptibility in ZFC and FC modes in 2–300 K temperature range as well as magnetization in magnetic fields up to 70 kOe have revealed complex magnetic behavior and transition to the antiferromagnetic phase below 2.7 K. The value of the effective magnetic moment calculated from static magnetization measurements was significantly smaller than expected from nominal valences of iron and copper ions indicating strong antiferromagnetic correlations and interactions in clusters or chains of magnetic ions even at high temperature. Although the paramagnetic phase covers a broad temperature range (3–300 K) it differs in many aspects at low and high temperatures. Temperature dependence of EPR parameters (*g*-factor, linewidth, integrated intensity) obtained by fitting the experimental spectrum with Lorentzian lineshape point to the presence of antiferromagnetic dimers in the high-temperature range, strong antiferromagnetic correlations in the paramagnetic phase and critical slowing down of the spin fluctuations on approaching Neel temperature as well as the appearance of magnetically isolated iron ions in the antiferromagnetic phase.

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1. Introduction

The compound $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ is a new vanadate, which has been obtained recently in the ternary oxide system $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ [1,2]. It is known that components of this system as well as phases forming in its side systems, are active in catalytic oxidation reactions of: benzene to phenol [3], methanol to formaldehyde [4], isobutane to isobutene [5], or toluene to benzaldehyde [6]. Therefore, the compound $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$, forming with an involvement of all components of the $\text{CuO-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ system, can be considered as the phase with potential catalytic properties. A comprehensive study of physicochemical properties of this new compound is very important to determine advantages and limitations of its applications.

Basic physicochemical characterization of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ has been already established [1]. This compound has a brown color, its density amounts to $3.97(5) \text{ g/cm}^3$, it crystallizes in the monoclinic system and melts incongruently at $790(5)^\circ\text{C}$ [1]. The IR spectrum and SEM image of this new compound have been already published [1]. The absorption bands located in the $1050\text{--}600 \text{ cm}^{-1}$

wave number range can be ascribed to the stretching vibrations of the V–O bonds in the VO_4 and VO_5 polyhedra or they can be due to the stretching vibrations of the Fe–O bonds in the FeO_5 and FeO_4 polyhedra [1]. Bands in $600\text{--}300 \text{ cm}^{-1}$ range can be associated with stretching vibrations of the metal–oxygen bonds within FeO_6 and CuO_x polyhedra as well as with bending vibrations of O–V–O bonds [1].

Up to now no magnetic measurements have been carried out on this new compound. As $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ contains magnetic ions it could display interesting magnetic characteristics. Very intriguing magnetic phenomena were found in other similar vanadate compounds [7–11]. It is also known from literature [12–18] that magnetic measurements are useful in catalytic investigations. As an example, catalytic activity of ferromagnetic or antiferromagnetic phases can change at the Curie or Neel temperatures. On the other hand, magnetic properties of the active phase can change during catalyst's work, especially during adsorption. Investigation of such changes can be helpful in determining the mechanism of the studied catalytic process.

In this work magnetic properties of a new double vanadate $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ in powder form are presented. The obtained results complete physicochemical characteristics of the new compound and they can be useful in its catalytic studies, which are planned.

Two complimentary methods of magnetic characterization

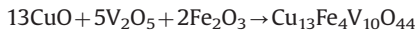
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were employed: dc magnetization measurements as a function of temperature and an external magnetic field, and electron paramagnetic resonance (EPR) study in the microwave frequency range. The obtained results will be discussed separately at first, and finally compared to obtain a comprehensive picture of magnetic properties of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ compound.

2. Experimental

The $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ compound has been obtained by a standard solid-state reaction method, according to the following equation:



The details of synthesis are described elsewhere [1]. The position of the $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ compound in the component concentration triangle of the CuO – V_2O_5 – Fe_2O_3 system is presented in Fig. 1.

The dc susceptibility measurements were carried out in the 2–300 K temperature range using an MPMS-7 SQUID magnetometer and in magnetic fields up to 70 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes. EPR study was performed on a conventional X-band ($\nu=9.4$ GHz) Bruker E 500 spectrometer with the 100 kHz magnetic field modulation. The measurements were carried in the 4–290 K temperature range using an Oxford Instrument helium-flow cryostat. The registered spectra were the first derivative of the absorption curve with respect to the sweeping external magnetic field.

3. Results and discussion

3.1. DC susceptibility and magnetization study

In Figs. 2–5 the temperature dependence of dc magnetic susceptibility $\chi(T)$ in ZFC mode is presented. In Fig. 2 this dependence in ZFC mode registered at four different external magnetic fields in the whole studied temperature range (2–300 K) is shown. Inset in Fig. 2 displays the low temperature $\chi(T)$ curves in an expanded scale. In Fig. 3 comparison between $\chi(T)$ curves in ZFC and FC modes is presented. As it is clearly seen both curves collapse and no irreversibility range is visible. In Fig. 4 temperature dependence of the reciprocal dc magnetic susceptibility $\chi^{-1}(T)$ in FC mode registered at four different magnetic fields is shown and the inset

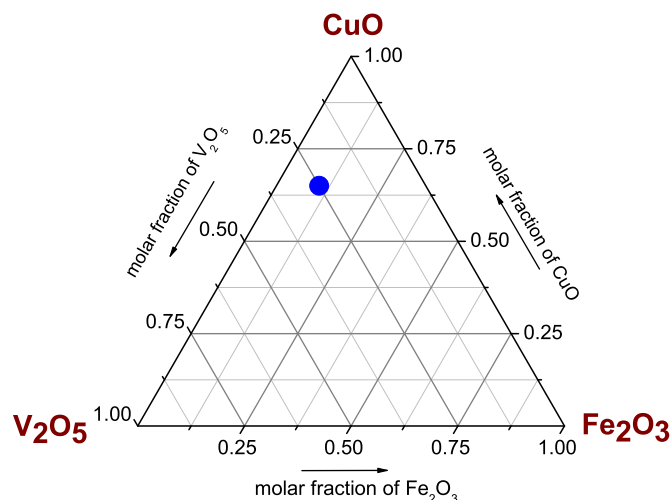


Fig. 1. The position of $\text{Cu}_{13}\text{Fe}_4\text{V}_{10}\text{O}_{44}$ compound in the component concentration triangle of the CuO – V_2O_5 – Fe_2O_3 system.

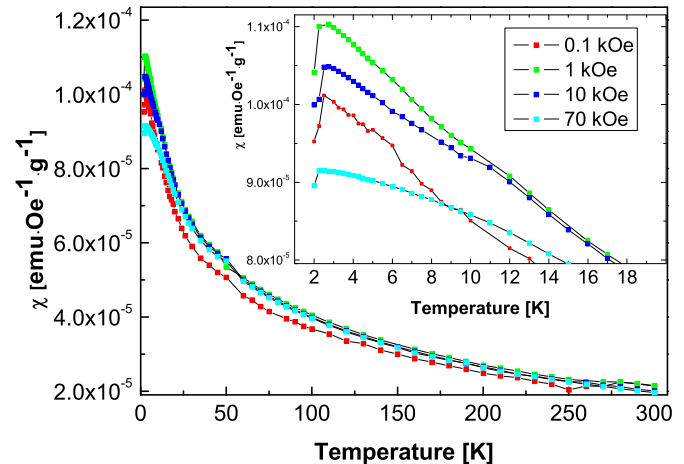


Fig. 2. Temperature dependence of dc magnetic susceptibility χ in ZFC mode registered at four different magnetic fields. Inset shows the low temperature $\chi(T)$ curves in an expanded scale.

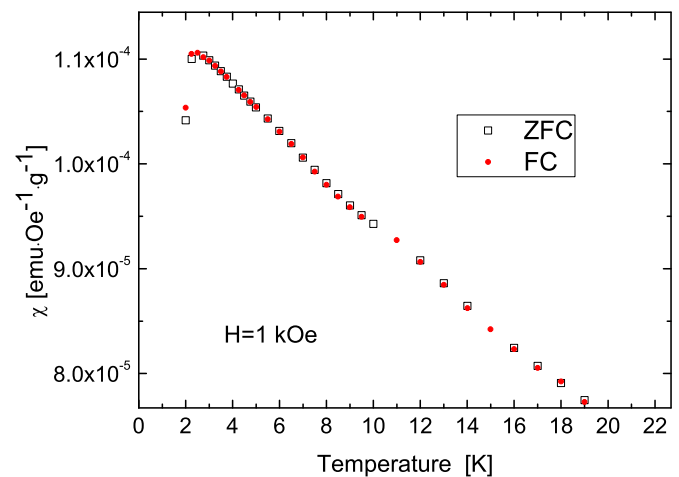


Fig. 3. Comparison of temperature dependence of magnetic susceptibility in ZFC and FC modes in low temperature range.

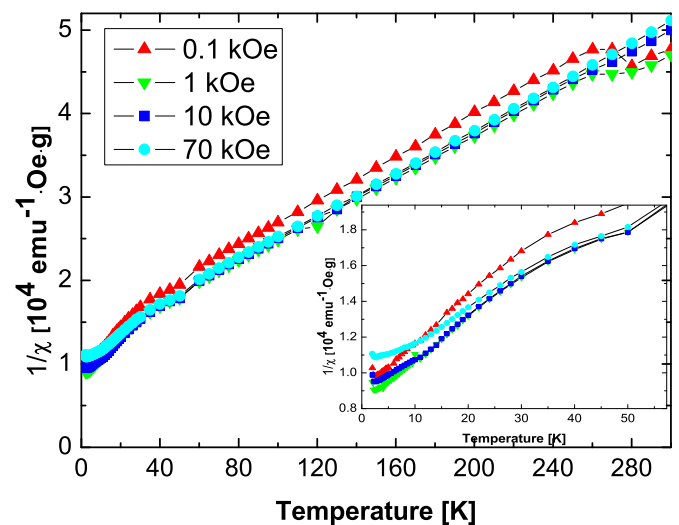


Fig. 4. Temperature dependence of reciprocal dc magnetic susceptibility $1/\chi$ in FC mode registered at four different magnetic fields. Inset shows the low temperature $\chi^{-1}(T)$ curves in an expanded scale.

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