Magnetic and Electrical Properties of Zn$_3$P$_2$ + MnP Materials

S. F. Marenkin$^{a,b}$, V. M. Trukhan$^c$, I. V. Fedorchenko$^a$, S. V. Trukhanov$^c$, and T. V. Shelkovaya$^c$

$^a$ Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

$^b$ Moscow Institute of Steel and Alloys (National University of Science and Technology), Leninskii pr. 4, Moscow, 119049 Russia

$^c$ Scientific–Practical Materials Research Centre, Belarussian Academy of Sciences, ul. Brovki 19, Minsk, 220072 Belarus

e-mail: marenkin@rambler.ru

Received October 24, 2012

Abstract.—We have synthesized a new ferromagnetic material based on a Zn$_3$P$_2$ + MnP composite with a Curie temperature of 290 K. Experimental data demonstrate that its magnetic and electrical properties are determined by manganese phosphide nanoclusters. The composite has metallic conductivity. Its electrical resistance drops with increasing magnetic field, and its magnetoresistance in a magnetic field of 14 T at 7 K reaches 9%.

DOI: 10.1134/S0020168513050087

INTRODUCTION

Advances in spintronics are highly dependent on the development of novel composite materials. Such materials are key components for the fabrication of magnetic memory devices, including spin valves and MRAM devices. These devices take advantage of structures made up of two ferromagnetic nanolayers and a nonmagnetic nanolayer in between. The fabrication of such multilayer structures presents a number of technological problems. This has aroused considerable interest in single-layer composite materials in which ferromagnetic nanoclusters are embedded in a nonmagnetic matrix. Such materials are referred to as granular structures. Figure 1 illustrates the mechanism underlying the magnetoresistance of such structures. In zero magnetic field, the magnetic moments of the ferromagnetic clusters are oriented at random. In an applied magnetic field, their magnetic moments align along the field and this leads to a significant change in the electrical resistance of the material.

The magnetoresistance is proportional to the external magnetic field, the cosine of the angles between the

![Fig. 1. Schematic of the mechanism underlying the magnetoresistance of a composite containing ferromagnetic clusters in a nonmagnetic matrix.](image-url)
magnetic moments, and the number density of the ferromagnetic clusters [1]. One advantage of composite materials is that their magnetoresistance develops not in a multilayer but in a single-layer structure. Such structures are more technologically attractive, but the ability to fabricate them requires a search for systems formed by a ferromagnet with a Curie point above room temperature and a nonmagnetic material. In addition, it is important that such phases form essentially no solid solutions. It seems likely that the optimal approach to creating such composites is to use eutectic systems with limited mutual solubility of their end-members.

Novotortsev et al. [2, 3] reported the preparation of new ferromagnets with high Curie temperatures and studied the nature of the magnetism in manganese-doped II–IV–V compounds. According to their results, the magnetic properties of such materials were determined by manganese pnictide (MnP, MnAs, or MnSb) nanoclusters. As shown by Kilanski et al. [4, 5], manganese-doped ZnGeAs2 and CdGeAs2 possess considerable magnetoresistance, which confirms the possibility of a colossal magnetoresistive effect in single-layer structures.

The subject of this study was a zinc phosphide/manganese phosphide (Zn3P2/MnP) composite. Zinc phosphide is a II–V semiconductor. As a material for solar power conversion applications, it can be prepared in thin film form through thermal evaporation in vacuum [6]. Manganese phosphide is a ferromagnet with a Curie temperature of 291 K. It exhibits a sizeable magnetoresistance, which confirms the possibility of a colossal magnetoresistive effect in single-layer structures.

The choice of Zn3P2 as the subject of this study was prompted by the fact that it can be prepared in thin film form through thermal evaporation in vacuum [8] and can, therefore, be considered a matrix for fabricating two-dimensional semiconductor–ferromagnet composite structures.

EXPERIMENTAL

Zn3P2 + MnP samples were prepared using the reaction 3Zn3P2 + 4Mn = Zn3P2 + 4MnP, which is more effective than elemental synthesis because of the high phosphorus volatility and the associated deviations from stoichiometry in the resulting materials.

The starting zinc diphosphide powder was prepared from ZnP2 single crystals grown by a procedure described elsewhere [9]. The manganese was purified by two vacuum sublimations. Weighed starting mixtures were placed in graphite-coated silica tubes, which were then pumped down to 10⁻² Pa and sealed off. The total weight of the starting mixtures was 10 g. The tubes were first heated to the melting point of ZnP2 and held there for 2 h. Next, the temperature was raised to the melting point of Zn3P2, and the melt was stirred by vibration for 3 h, followed by rapid cooling of the tubes.

The resultant samples were characterized by X-ray diffraction at room temperature on DRON-2 and DRON-3 diffractometers with CuKα (λ = 0.154051 nm) and CrKα (λ = 0.228962 nm) radiations. X-ray diffraction data were analyzed by the Rietveld and Le Bail methods using FullProf software.

Figure 2 shows the X-ray diffraction pattern of the synthesized samples. The observed diffraction peaks indicated that the only phases present were MnP and Zn3P2. Their contents were determined to be 57 and 43%, respectively, in good agreement with the starting-mixture composition (56.92% MnP and 43.08% Zn3P2). Spark source mass spectrometry results for the synthesized samples confirmed the X-ray diffraction data. The content of elements other than Mn, P, and Zn was within 0.01 wt %.

The magnetic properties of the samples were studied in the temperature range 5–310 K at magnetic inductions from 0.01 to 14 T using a SQUID vibrating sample magnetometer (Cryogenics). The magnetic measurement procedure was based on the inductive principle of magnetic moment measurements through measurements of the ac electromagnetic field of a vibrating magnetic sample.

The electrical resistance of the samples was measured by the four-probe method at electrical currents within 10 mA. Ohmic contacts to the samples were made by indium solder using a UZP-2 ultrasonic soldering iron and UZG-4 generator.

Figure 3 shows the temperature dependences of magnetization for the Zn3P2 + MnP composite in magnetic fields of 0.01 and 0.1 T, which are very similar to the temperature dependences of magnetization characteristic of manganese phosphide. According to Reis et al. [7] and Aitken et al. [10], the sharp increase in magnetization at a temperature near 50 K is caused by the transition of MnP from a metamagnetic state (with a double-helix magnetic structure) to a ferromagnetic one. The high-temperature drop in magnetization can be accounted for by the transition of MnP from the ferromagnetic state to a paramagnetic one. Its Curie temperature is near 290 K. The temperature variation of its magnetization leads us to conclude that the magnetic properties of the composite are determined by the manganese phosphide.

The magnetic field dependence of 7-K magnetization for the Zn3P2 + MnP composite in the range 0–10 T (Fig. 4) shows an S-shaped magnetic hysteresis, characteristic of polycrystalline manganese phosphide and due to the metamagnetic state of the MnP [7, 10].