

Thermodynamics properties of $\text{NiCuP}_4\text{O}_{12}$

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Abstract

The variation of magnetic susceptibility and heat capacity with temperature for the bimetallic nickel Ni(II)–copper Cu(II) cyclo-tetrametaphosphates ($\text{CuNiP}_4\text{O}_{12}$) has been examined. The complex has a structure of quasi-one-dimensional alternate spins chains of Ni(II) and Cu(II) that exhibits a three-dimensional magnetic ordering at approximately 13.5 K. The compound is characterized by a ferromagnetic intrachain constant $J_F = 4.05$ K, with a significant effect of single ion anisotropy $D = 9.70$ K. The chains are weakly coupled antiferromagnetically with an interchain exchange constant of $2z_{AF}J_{AF} = -1.125$ K.

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1. Introduction

The variation of magnetic susceptibility with temperature gives valuable information about the structure and its thermal transitions for metallic compounds such as phosphates and vanadium oxides. Qualitative and quantitative correlations between various structural features and magnetic behavior have been postulated for such materials [1]. Among these compounds, the so-called low-dimensional (i.e. clusters, chains or layers) structures show unusual phenomena [2,3] with many potential technological applications.

In this paper, we present the thermodynamics properties of $\text{NiCuP}_4\text{O}_{12}$. This well-known cyclo-tetrametaphosphate, also used as pigment, has to our knowledge, never been investigated for its quantum magnetic properties. The structure is built up from corrugated two distinct metal-oxygen octahedral ($10\bar{1}$) chains. The $\text{P}_4\text{O}_{12}^{4-}$ anions bridge the neighboring chains together and ensure the three-dimensional (3D)

stability. The metals' electronic configurations are $3d^8$ (Ni^{2+} , $S=1$ and Cu^{2+} , $S=1/2$).

We show that the dimensionality of the magnetic interaction lattice defined by the different magnetic couplings between the spins is intermediate between 1D and 2D. Taking into account the principal magnetic interactions, the structure appears to be quasi-2D consisting, within ($10\bar{1}$), a set of parallel alternating spin chains connected by weak interchains coupling.

As a part of our research in the field of phosphate, vanadate and low-dimensional systems [4–7], we report here on the magnetic susceptibility and specific heat measurements together with the determination of exchange interaction and Landé factor.

2. Experimental

$\text{NiCuP}_4\text{O}_{12}$ compound was synthesized by solid-state reaction in air starting from $\text{Ni}_2\text{P}_4\text{O}_{12}$ and $\text{Cu}_2\text{P}_4\text{O}_{12}$. Stoichiometric quantities of the materials were ground together in an agate mortar. The resulting mixture was heated in a Pt crucible at 450°C for 48 h with an intermediate regrinding using the procedure described in

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Ref. [8]. The crystal structure and the lattice constants were determined by the X-ray powder diffraction (XRD) method using Cu K α radiation at room temperature.

Magnetic susceptibility measurements have been performed in the temperature range 2–300 K with a Faraday-type magnetometer (applied field $H = 12,800$ Oe).

Low-temperature specific heat measurements have been performed in the temperature range 1.2–35 K using a quasi-adiabatic measurement setup. The chamber contains a sapphire sample holder equipped with a Ge resistance thermometer and an evaporation deposit Cr/Ti heater. The accuracy of measurements is 1% (for samples of about 0.5 g) after subtracting the specific heat of the addenda.

3. Results and discussion

3.1. Description of structure

The obtained bimetallic compounds belong to the isostructural series of general formulation $M_1M_2PO_{12}$, where $M_i = \text{Co}, \text{Zn}, \text{Mg}$ [9–12]. In the present case, $M_1 = \text{Ni}$ and $M_2 = \text{Cu}$. The XRD measurements, using Cu K α radiation of $\text{NiCuP}_4\text{O}_{12}$ indicates that this compound is isostructural with $\text{NiMP}_4\text{O}_{12}$ ($M = \text{Co}, \text{Zn}$) [13]. The structural parameters were refined by the Rietveld method. Indexing Bragg reflections in the XRD data indicated that $\text{NiCuP}_4\text{O}_{12}$ crystallizes in the monoclinic system with lattice parameters of $a = 12.549$ Å, $b = 8.083$ Å, $c = 9.562$ Å, $\beta = 118.45^\circ$, $Z = 4$. The structure was successfully solved in the space group $C2/c$. The structure may be roughly described as infinite zigzag chain made of alternating metal ions M_1 and M_2 involved in two distinct MO_6 octahedron linked by edge, and two kinds of PO_4 tetrahedron forming $\text{P}_4\text{O}_{12}^{4-}$ anions. M_1 and M_2 are characterized by one- and two-point symmetry, respectively [9]. The $(M_2)\text{O}_6$ octahedron is slightly larger than $(M_1)\text{O}_6$ and displays a larger scatter in M–O distance and O–M–O angles. With regard to the coordination geometry, both the Ni and Cu ions could have an octahedral coordination of the ions. The Cu^{2+} ions are known to prefer the $(M_2)\text{O}_6$ octahedron while the Ni^{2+} ion prefer $(M_1)\text{O}_6$. The main differences in the topology of the chain are due to the cation radii $r_{\text{Ni}^{2+}} = 0.70$ Å and $r_{\text{Cu}^{2+}} = 0.73$ Å. Thus as stipulated by Nord [13], one may expect that the substitution of 50% of nickel in $\text{Ni}_2\text{P}_4\text{O}_{12}$ for 50% copper would lead to an order and alternating metallic chain.

The structure of $\text{NiCuP}_4\text{O}_{12}$ corresponds to a site alternation within a given chain with Ni(II) and Cu(II) occupying inequivalent $(M_1)\text{O}_6$ and $(M_2)\text{O}_6$ positions, respectively; each one is bridged to its neighbors by two oxygen groups. Ni^{2+} is ordered at smaller and more regular M_1 sites and Cu^{2+} at the M_2 sites [9] (Fig. 1).

Thus, the structure will be described as infinite zigzag chains of alternating $S_a = 1$, $S_b = 1/2$ spins giving rise to bimetallic ordered chain. The alternating spin chain may then be schematically illustrated as $(\text{Ni})\text{O}_6\text{--}(\text{Cu})\text{O}_6\text{--}$

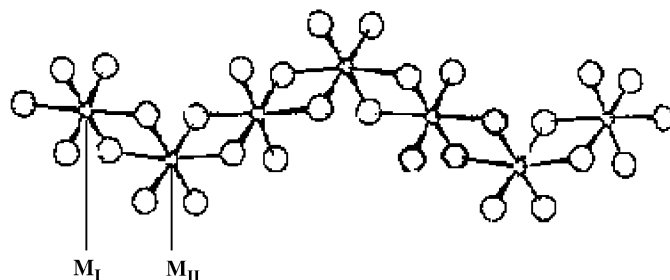


Fig. 1. Sketch of the chain, projection on $(10\bar{1})$ plane (Ref. [9]).

$(\text{Ni})\text{O}_6\text{--}(\text{Cu})\text{O}_6$ parallel to $10\bar{1}$. Such a structure is well adapted for magnetic modeling.

3.2. Magnetic behavior

Fig. 2 shows the temperature dependence of molar magnetic susceptibility data for the sample cooled in 12,800 Oe. The susceptibility data exhibit Curie–Weiss paramagnetism down to a temperature T_{max} , at which the sample turns antiferromagnetic. Thus the maximum in the magnetic susceptibility is observed at $T_N = 14.5$ K, which is typical of 3D antiferromagnetic ordering. A very small increase in χ at temperatures below T_N is inferred to the presence of a small amount of paramagnetic impurities.

The susceptibility data can be fitted by the Curie–Weiss equation $\chi_m = C_m/(T-\theta)$, where C is the Curie constant, T the temperature and θ the Weiss constant. The best linear curve fitting to the susceptibility in the temperature range (70–300 K) yields the followings values $C_m = 1.52$ emu K/mol and $\theta = 3.5$ K, which indicate that the dominant magnetic exchange interactions are ferromagnetic.

The plot of $\chi_m T$ vs T for $\text{NiCuP}_4\text{O}_{12}$ is shown in Fig. 3. The most notable feature is the broad maximum around 23.53 K from 300 to 23.53 K, where the value of $\chi_m T$ increases upon lowering the temperature. This behavior is characteristic of the presence of dominant ferromagnetic intrachain interactions. At 300 K, the calculated effective magnetic moment is $3.66\mu_B$, which is higher at high temperature than the value of $3.31\mu_B$ expected for such combinations of free Cu(II) and Ni(II). This experimental high value is also consistent with the presence of intrachain ferromagnetic coupling between nickel and copper. The peak at 23.53 K together with the reduction of $\chi_m T$ on cooling below 23.53 K is consistent with the onset of interchain antiferromagnetic interactions. Such results indicate that we are dealing here with both ferromagnetic and antiferromagnetic interactions.

At high temperatures, an increase of magnetic moment suggests intramolecular ferromagnetic interaction between nickel and copper ions in the polymeric chain. From the structural information, we know that the compound is polymeric and there are two non-equivalent M(II) sites, both located at non-equivalent symmetry centers. The Dzialoshinsky–Moriya exchange mechanism operates and the structure is canted, giving rise to weak ferromagnetic

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