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MAGNETIC PROPERTIES OF TRANSITION-METAL TETRAMETAPHOSPHATES

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Abstract. – We investigated powder samples of the tetrametaphosphates $M_2P_4O_{12}$ (M = Mn, Co, Ni, Cu) by magnetic measurements and neutron diffraction down to 1.7 K. Except for the Cu compound we found Néel temperatures and overall antiferromagnetic LRO. The Mn isomorph shows 1D-Heisenberg behaviour. $Ni_2P_4O_{12}$ undergoes a spin-flop, $Co_2P_4O_{12}$ a two-step metamagnetic transition.

Introduction

The tetrametaphosphates $M_2P_4O_{12}$ of divalent cations crystallize in the monoclinic space group C2/c [1]. The metal ions M, octahedrally coordinated by oxygen, form characteristic zigzag chains in the [101] direction that are separated by P_4O_{12} rings (Fig. 1). There are two nonequivalent lattice sites I and II alternating within the chains. Since the intra-chain distance (≈ 300 pm) is smaller than the inter-chain distance (≈ 500 pm) quasi-one-dimensional (1D) magnetic behaviour was anticipated.

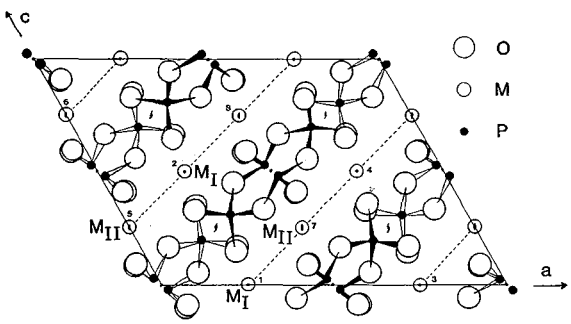

Fig. 1. – Projection of the unit cell of the tetrametaphosphates on the (010) plane (after Laügt *et al.* [1]).

Experimental

We prepared powder samples of $M_2P_4O_{12}$ with M = Mn, Co, Ni, and Cu after Thilo and Grunze [2], but we could not prepare pure $Fe_4P_4O_{12}$, yet. The growth of single crystals is under way.

Magnetic measurements were performed using a SQUID type susceptometer in a temperature range of 2 K to 400 K. The magnetic fields applied were 500 Oe for susceptibility measurements and up to 50 kOe for magnetization measurements.

Neutron diffraction experiments were carried out with a position sensitive detector powder diffractometer at the SILOE reactor of the Centre d'Etudes Nucléaires de Grenoble (CENG) in Grenoble, France, between 1.7 K and 100 K. The magnetic structure results will be published elsewhere [3].

Results and discussion

$Mn_2P_4O_{12}$: deviations from Curie-Weiss behaviour were found below 35 K, whereas a transition to long range magnetic order (LRO) occurred at only 3.2 K. A negative paramagnetic Curie temperature (Θ_p = −16(2) K) and a negative curvature of $\chi.T$ *vs.* T indicate antiferromagnetism, in agreement with the neutron scattering results [3, 5]. A further increase of the susceptibility below T_c is regarded as an impurity contribution. We assumed Curie paramagnetism for this portion, and after its subtraction a broad maximum in $\chi(T)$ remained, which could be fitted by a 1D Heisenberg model with an exchange constant $J/k = -1.04$ K (Fig. 2).

$Co_2P_4O_{12}$: deviations from Curie-Weiss behaviour were observed below 180 K, but LRO did not occur before 8.1 K. Again a negative curvature of $\chi.T$ and a negative (though not significant) Θ_p = −7(10) K

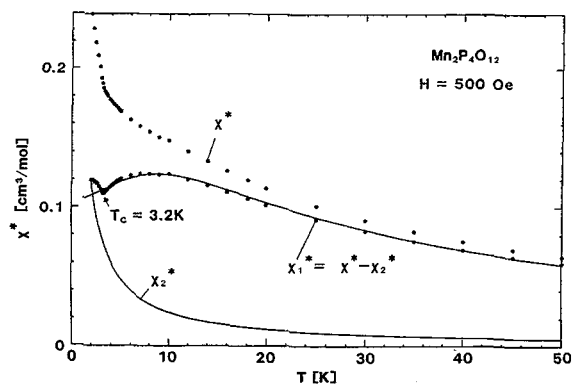

Fig. 2. – Magnetic susceptibility of $Mn_2P_4O_{12}$ χ: as measured; χ_2 : paramagnetic contribution; $\chi_1 = \chi - \chi_2$: result after subtraction of paramagnetic portion; solid line: fit of the $S = 5/2$ 1D-Heisenberg model susceptibility to χ_1, $J = -1.04$ K.

indicated antiferromagnetism which was confirmed by neutron scattering [3, 5]. Below T_c $\chi(T)$ decays exponentially according to

$$\chi(T) \sim \exp(-19.3\ K/T) + \text{const.},$$

which is typical for 3D Ising behaviour [4]. This is confirmed by the fact that χ decays to a value much lower than $2/3\chi(T_c)$, indicating a strong anisotropy at T_c.

Below 6.1 K the magnetization curves of $Co_2P_4O_{12}$ show two inflection points, leading to a magnetic phase diagram displayed in figure 3. We interpret this as a two-step metamagnetic transition with an intermediate ferrimagnetic phase.

$Ni_2P_4O_{12}$: from a plot of χ *vs.* $1/T$ we determined a temperature independent paramagnetism (TIP) of $2.1(5) \times 10^{-4}$ cm^3/mol. Curie-Weiss behaviour was observed down to 170 K, the Néel point was found at 13.5 K. In this case Θ_p is approximately zero, and a positive curvature of $\chi.T$ *vs.* T above 25 K indicates dominating ferromagnetic interaction. If a dominating intra-chain interaction is assumed, this is in agreement with the magnetic structure results (overall antiferromagnetic structure, but ferromagnetic chains [3, 5]).

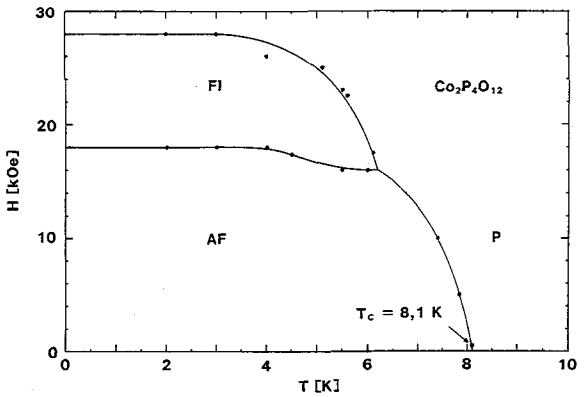

Fig. 3. – Magnetic phase diagram derived from magnetization measurements on $Co_2P_4O_{12}$ powders; P = paramagnetic, AF = antiferromagnetic, FI = ferrimagnetic, SP = saturated-paramagnetic. The solid lines are just guidelines to the eye.

$Cu_2P_4O_{12}$: this compound showed an unusually large TIP: $9.1(6) \times 10^{-4}$ cm^3/mol. After its subtraction Curie-Weiss behaviour reached down to 160 K. Θ_p could not be determined exactly (3 ± 42 K), but the negativ e curvature of $\chi.T$ indicates a tendency towards antiferromagnetism. However, neutron diffraction did not show any transition to LRO down to 1.7 K [6]. A Curie point-like anomaly in χ at 7.9 K is probably due to an impurity.

Conclusion

All transition metal tetrametaphosphates investigated display overall antiferromagnetic behaviour. Except for the Cu compound we found Néel points at a few Kelvins. Only $Mn_2P_4O_{12}$ shows quasi-one-dimensional magnetic properties, though in all compounds χ deviated from Curie-Weiss behaviour already at temperatures much larger than T_c. For $Ni_2P_4O_{12}$ and $Cu_2P_4O_{12}$ we found TIP.

Acknowledgment

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