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Synthesis and Magnetic Properties of Transition Metal Cyclotetraphosphates $M_2P_4O_{12}$ (M = Mn, Co, Ni, Cu)

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Polycrystalline samples of isomorphous divalent metal cyclotetraphosphates $M_2P_4O_{12}$ (M = Mn, Co, Ni, and Cu) were prepared and their magnetic properties investigated. The compounds were further analyzed by X-ray diffraction, ESR spectroscopy, and neutron diffraction. For the Mn, Co, and Ni compounds, below the Néel temperatures of T_N = 3.2, 8.1, and 13.5 K, overall antiferromagnetic ordering was found. The susceptibility of $Mn_2P_4O_{12}$ is interpreted in terms of a one-dimensional Heisenberg $S = 5/2$ model with antiferromagnetic nearest-neighbor interaction ($J/k_B = -1.0(1)$ K). Cobalt and nickel cyclotetraphosphate do not exhibit quasi-one-dimensional magnetic behavior. Magnetization measurements revealed a spin–flop transition of $Ni_2P_4O_{12}$ and a two-step metamagnetic phase transition for $Co_2P_4O_{12}$. $\chi(T)$ diagrams of the cobalt compound indicate a strong anisotropy of susceptibility. No magnetic long-range order was observed by ESR and neutron diffraction in the case of $Cu_2P_4O_{12}$ down to 1.7 K. ESR spectra showed exchange-narrowing at room temperature for the manganese compound and below 7.9 K for the copper compound.

Introduction

Low-dimensional and quasi-low-dimensional magnetic systems have been the subject of intense theoretical and experimental research during the last two decades (cf., e.g., (*1*, *2*)). In search of new quasi-one-dimensional (1D) compounds, we have investigated the isomorphous cyclotetraphosphates of Mn, Co, Ni, and Cu, which exhibit zigzag chains of cations as one important structural feature (*3*), in contrast to many 1D magnetic systems already studied (*1*).

Crystal structure data of several divalent metal cyclotetraphosphates are reported in the literature (*3–9*). Rohwer *et al.* (*10*) refined the atom positions in $Mn_2P_4O_{12}$ using neutron diffraction. These compounds crystallize in the monoclinic space group *C2/c*. Each metal ion is octahedrally coordinated by exocyclic oxygens of the cyclotetraphosphate anions whereby the octahedra share edges to form zigzag chains of cations. The unit cell contains four formula units with two nonequivalent lattice sites

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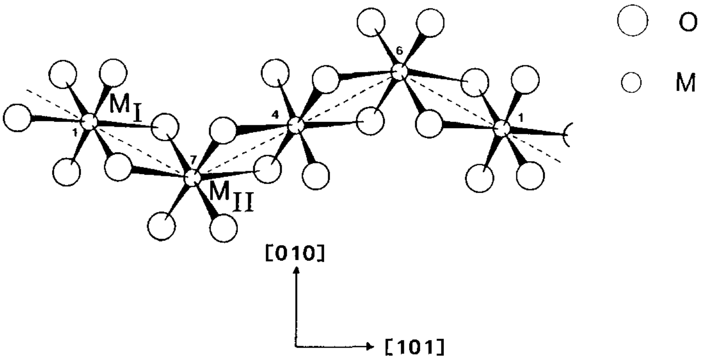

FIG. 1a. Projection of a chain of cations—octahedrally coordinated by oxygen—on the $(10\bar{1})$ plane (after Laügt *et al.* (*3*)).

for the metal ions designated by **I** and **II** (see Fig. 1a). The chains are separated by layers of cyclotetraphosphate rings as shown in Fig. 1b. A strong distortion of the MO_6 octahedra was found for the Cu compound only and can be attributed to a Jahn–Teller effect. The nearest-neighbor distance within the chains is about 330 pm for all compounds. The interchain distances are approximately 500 pm between M_{II} sites and 540 pm between M_I and M_{II} sites. The next-nearest-neighbor distance between M_I ions within a chain is circa 570 pm, so that an interaction between them is expected to be of the same order of magnitude as the interchain interaction (*11*).

Synthesis

Polycrystalline samples of cyclotetraphosphates $M_2P_4O_{12}$ (M = Mn, Co, and Ni) were prepared from a mixture of aque-

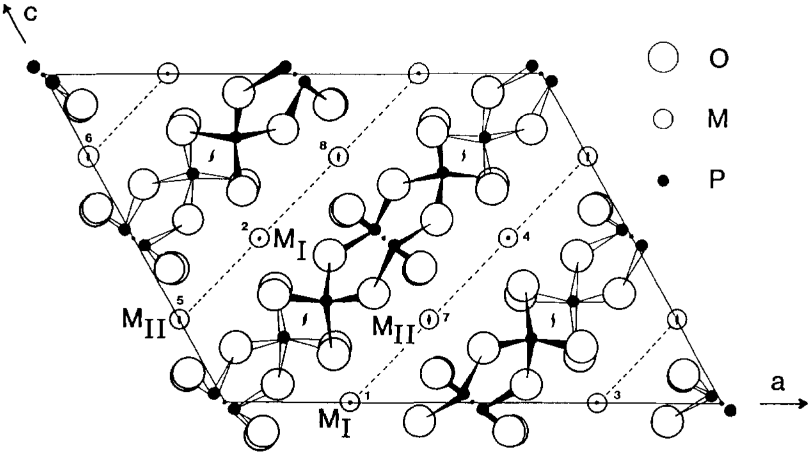

FIG. 1b. Projection of the unit cell of $M_2P_4O_{12}$ on the (010) plane (*3*). Different lattice sites of the cations are designated by **I** and **II**.

ous H_3PO_4 (85% by weight) and the corresponding metal chloride MCl_2 according to a method previously described by Thilo and Grunze (*12*). The mole ratio $n_{H_3PO_4}/nMCl_2$ was 2.4. The first step was a thermal treatment of the well-homogenized mixture until the formation of HCl was no longer observed. The second was the calcination of the resulting dihydrogenmonophosphates for 20 hr at 720 K in a platinum–gold crucible. After cooling to room temperature, the sample was washed with deionized water and subsequently dried at 370 K. The reaction of H_3PO_4 with metal oxides as opposed to metal chlorides did not yield pure samples.

Additionally, cobalt and manganese cyclotetraphosphates were prepared at lower reaction temperatures down to 575 K (cf. (*13*)). The products obtained had to be stirred with aqueous 4 *M* HCl for 20 hr at room temperature and subsequently washed with water and acetone to yield pure cyclotetraphosphates.

Powder samples of copper cyclotetraphosphates were prepared by evaporating a solution containing a slight excess (105% of the stoichiometric amount) of H_3PO_4 with copper dichloride dihydrate, followed by heating the mixture at 730 K for 5 hr in a platinum–gold crucible with a heating rate of 150 K/hr (*14*). The products were cooled to room temperature and washed with water. The samples prepared after this method contained about 10% of copper diphosphate $Cu_2P_2O_7$, which was identified by X-ray diffraction. Pure $Cu_2P_4O_{12}$ samples were prepared using an improved method: doubling the amount of H_3PO_4 inhibits the formation of $Cu_2P_2O_7$.

Experimental

Magnetic measurements were carried out using a Faraday balance within a temperature range from 5 to 270 K and a SQUID-type susceptometer (SHE VTS 905) between 2 and 400 K. The fields applied were 40 kA m^{-1} for susceptibility measurements and up to 4000 kA m^{-1} for magnetization measurements.

ESR spectra were recorded with an X-band spectrometer at 9.45 GHz (Bruker ER 220D) and at 9.21 GHz (Bruker ER 420) from 1.7 to 290 K.

Neutron diffraction experiments were performed using a powder diffractometer at the SILOE reactor of the Centre d'Etudes Nucleaires de Grenoble (CENG) in Grenoble, France. This instrument is equipped with a position-sensitive detector (*15*) that covers an angle range of $\Theta = 3° \ldots 43°$ with a resolution of 0.05°. During the measurements the wavelength was adjusted to 248.3 pm. Scattering diagrams were taken between 100 and 1.7 K for each sample.

Results and Discussion

1. Neutron Diffraction and Magnetic Measurements

1.1. Manganese cyclotetraphosphate. The temperature dependence of the reciprocal susceptibility follows a Curie–Weiss law above 35 K, leading to a negative paramagnetic Curie temperature $\Theta = -16(2)$ K. From this value and the negative curvature of χT vs T, antiferromagnetic ordering at low temperatures has been anticipated. This is confirmed by neutron scattering results, which show a long-range 3D antiferromagnetic order below $T_N = 3.2$ K. The magnetic susceptibility of manganese cyclotetraphosphate increases rapidly with decreasing temperature below T_N. This is attributed to a paramagnetic contribution. The occurrence of weak ferromagnetism is ruled out due to the absence of hysteresis in the magnetization curves (*11*).

The paramagnetic contribution is ascribed to impurities, which may be other phases as well as lattice defects such as voids or single Mn(IV) ions. For the paramagnetic contribution, designated by χ_2, a Curie law is assumed:

$$\chi(T) = \chi_1(T) + \chi_2(T) \tag{1}$$

with

$$\chi_2(T) = C_2/T. \tag{2}$$

In order to obtain C_2, χT vs T was plotted for $T < T_N$ and extrapolated to $T = 0$ K. Subtracting $\chi_2(T)$ from the measured susceptibilities over the whole temperature range yields a curve of $\chi_1(T)$ in accordance to that of a quasi-one-dimensional antiferromagnetic $S = 5/2$ Heisenberg model system. A more exact fit of a sum of the theoretical susceptibility for this model (*16*)

$$\chi_1(T) = C_1/T(1 + u)/(1 - u) \tag{3}$$

with

$$C_1 = Ng^2\mu_B^2\mu_0 S(S + 1)/3k, \tag{4}$$

$$u = \coth K - 1/K \tag{5}$$

$$K = 2JS(S + 1)/kT \tag{6}$$

and a Curie law according to Eq. (2) yields

$$C_1 = 4.69 \times 10^{-5}\ \mathrm{m^3\ K\ mole^{-1}} \tag{7}$$

$$J/k = -1.04(10)\ \mathrm{K}, \tag{8}$$

$$C_2 = 0.30 \times 10^{-5}\ \mathrm{m^3\ K\ mole^{-1}}. \tag{9}$$

The results are displayed in Fig. 2 (*11*, *17*).

The magnetization curve $M(H)$ at $T = 2$ K exhibits after subtraction of the paramagnetic contribution a saturation above $H = 240\ \mathrm{kA\ m^{-1}}$. The observed value of M ($H > 240\ \mathrm{kA\ m^{-1}}$) $= 0.4\ \mu_B$ corresponds closely to the difference between the magnetic moment of the Mn(II) ions located on the two nonequivalent sites M_I ($m_I = 3.55\ \mu_B$) and M_{II} ($m_{II} = 3.04\ \mu_B$) as obtained from neutron diffraction at 1.7 K (*11*). In fact, the spin arrangement within the chains is antiferromagnetic, the moments being roughly parallel to each other and perpendicular to the chain direction. The ratio of the coupling constants $J_{\mathrm{intrachain}}/J_{\mathrm{interchain}}$ is estimated at about 10. At low external field ($H < 240\ \mathrm{kA\ m^{-1}}$) the weak interchain coupling is easily broken, leading to the ob-

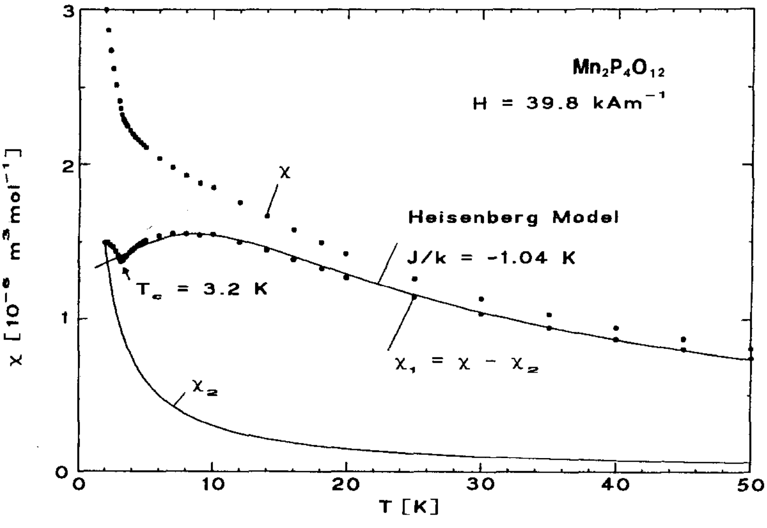

FIG. 2. Magnetic susceptibility of $Mn_2P_4O_{12}$. χ: measured values; χ_2: paramagnetic contribution; $\chi_1 = \chi - \chi_2$: susceptibility after subtraction of paramagnetic contribution; solid line: fit of the Heisenberg model susceptibility to χ_1 (*16*).

TABLE I

NUMERIC RESULTS OF MAGNETIC MEASUREMENTS

	$Mn_2P_4O_{12}$	$Co_2P_4O_{12}$	$Ni_2P_4O_{12}$	$Cu_2P_4O_{12}$
Spin	5/2	3/2	1	1/2
T_c	3.2(2) K	8.1(2) K	13.5(2) K	<1.7 K (?)
TIP [10^{-9} m^2/mole]	—	—	2.6(6)	—
Fit range for Curie–Weiss law	35 K . . . 400 K	180 K . . . 400 K	170 K . . . 400 K	160 K . . . 400 K

served low-field susceptibility. In an external field of $H > 240$ kA m^{-1} the alternating Mn moments within a chain remain coupled antiferromagnetically, thus giving rise to a noncompensated spontaneous magnetization.

1.2. Cobalt cyclotetraphosphate. The susceptibility of $Co_2P_4O_{12}$ obeys a Curie–Weiss law down to 180 K with the parameters shown in Table I. Below $T_{crit} = 8.1$ K the powder susceptibility decreases to a value of only 1/3 $\chi(T_{crit})$, indicating a strong anisotropy of χ even at T_{crit}. Below 7 K $\chi(T)$ follows the exponential law:

$$\chi(T) \sim \exp(-19.3\ \mathrm{K}/T) + \mathrm{const.} \quad (10)$$

This behavior is predicted theoretically for a 3D Ising system with antiferromagnetic nearest-neighbor coupling (*1*). A dominating antiferromagnetic interaction is indicated by a negative curvature of χT vs T for the greater part of the temperature range. However, in the range 20–30 K a ferromagnetic contribution can be suspected (see Fig. 3a).

In the magnetization curves two inflection points occur below 6.1 K. These features are due to a two-step metamagnetic

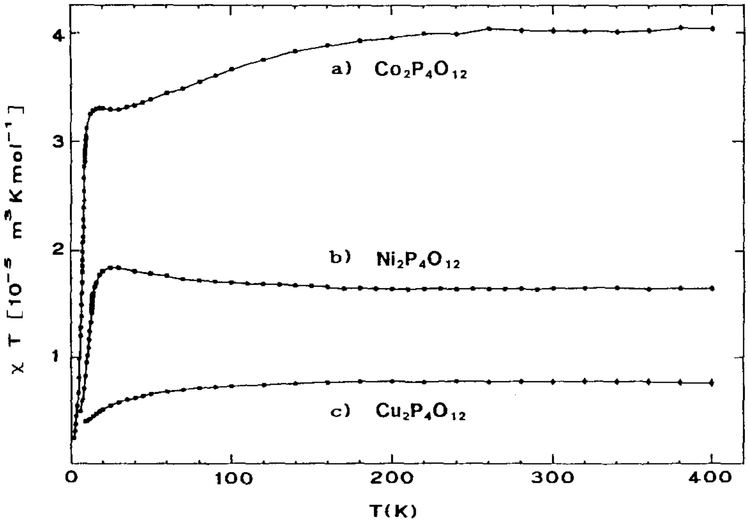

FIG. 3. (a–c) χT vs T diagrams of $M_2P_4O_{12}$. (a) M = Co; diagrams after subtraction of temperature independent paramagnetism (TIP) for (b) M = Ni and (c) M = Cu.

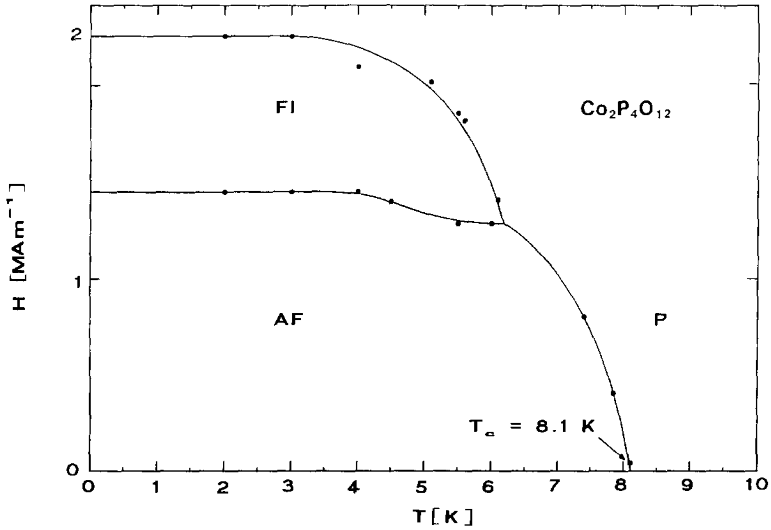

FIG. 4. Magnetic phase diagram of $Co_2P_4O_{12}$. AF, antiferromagnetic; FI, ferrimagnetic; P, paramagnetic phase.

phase transition with an intermediate ferrimagnetic phase. The magnetic phase diagram of $Co_2P_4O_{12}$ is displayed in Fig. 4. Neutron diffraction results show that ferromagnetic interactions exist within the chain, and antiferromagnetic ordering exists between them, the moments $m_I = 3.81$ μ_B and $m_{II} = 2.70$ μ_B being strongly different in magnitude and direction.

Further investigations of the structure and magnetic properties concerning diluted polycrystalline samples $M_{(2-x)}Mg_xP_4O_{12}$ and undiluted single-crystal samples are in progress (*18*).

1.3. Nickel cyclotetraphosphate. Overall antiferromagnetic structure with ferromagnetic intrachain interaction was established by neutron diffraction. Magnetic moments ($m_I = 2.23$ μ_B and $m_{II} = 2.16$ μ_B) within chains are parallel to each other and perpendicular to the chain direction. The positive curvature of χT vs T indicates contributions of ferromagnetic interaction above 25 K (see Fig. 3b). Magnetic susceptibility measurements as well as neutron diffraction results confirm a Néel point at 13.5 K (see Table I). From χ vs $1/T$ curves, a temperature-independent paramagnetism (TIP) of $2.6(6) \times 10^{-9}$ m³/mole was determined. The Curie–Weiss law is obeyed down to 170 K. An inflection point, evident in the magnetization curve at 2 K for a magnetic field of $H = 2.63(8) \times 10^6$ A/m, can be interpreted as a spin–flop transition.

1.4. Copper cyclotetraphosphate. Neutron diffraction studies did not show any long-range order down to 1.7 K. At 7.9 K a spontaneous magnetization and a Curie-point-like anomaly of the $\chi(T)$ curve occurs (Fig. 5, Table I).

2. ESR Spectroscopy

At room temperature, ESR signals of the Cu and Mn compounds are observed, whereas no signal is obtained from the Co and Ni compounds. In the case of $Ni_2P_4O_{12}$ ESR signals were found in the temperature range between 45 and 180 K (*18*).

2.1. Copper cyclotetraphosphate. The *g*-values of the powder spectra were assigned as described previously by Kneubühl and Taylor *et al.* (*19, 20*).

The Cu^{2+} ion is subject to a strong Jahn–Teller effect. The twofold orbital degener-

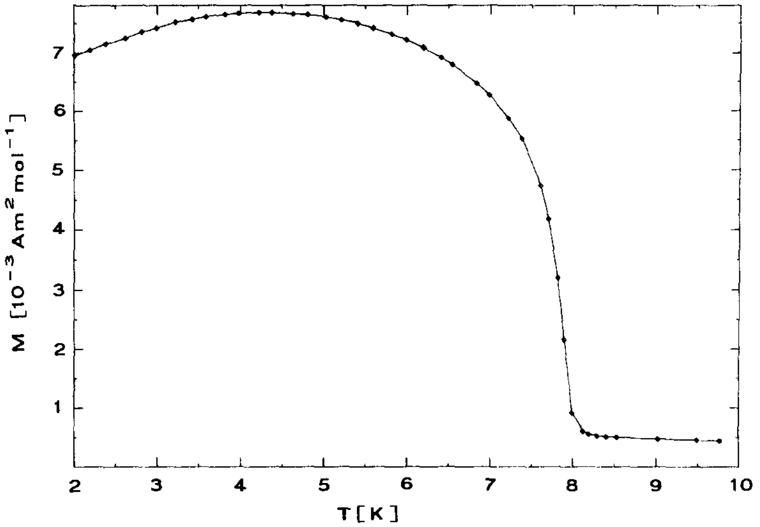

FIG. 5. Spontaneous magnetization of $Cu_2P_4O_{12}$.

acy is split by tetragonal or orthorhombic distortions, leaving a Kramers' doublet as the new energetically stabilized ground state. This ground state induces two or three different g-values. For tetragonal compression or elongation the following g-values are obtained (*21, 22*):

elongation

$g_{\parallel} = g_0 + 8u_{\parallel}$ $\quad g_{\perp} = g_0 + 2u_{\perp}$

compression

$g_{\parallel} = g_0$ $\quad g_{\perp} = g_0 + 6u_{\perp}$

$u_i = k_i\lambda/E_i$ (k, covalency constant; λ, LS coupling constant; E, cubic splitting of the ^2D ground state of the free Cu^{2+} ion).

The ESR spectrum of $Cu_2P_4O_{12}$ at room temperature shows a tetragonal g-tensor with $g_{\parallel} = 2.47$ and $g_{\perp} = 2.07$. These values are typical for a tetragonal elongation of the CuO_6 octahedra and in agreement with the X-ray structure analysis of Laügt *et al.* (*3*). Upon cooling, the spectrum did not change and no phase transitions were found between room temperature and 11 K. However, below 11 K the spectrum changed slowly and below 8 K drastically (see Fig. 6a–6c). At 2 K the following g-values were found:

$$g^{\perp} = 2.26 \quad g^{\parallel} = 2.09.$$

For the given geometry of edge-linked octahedra these g-values can be calculated (*23*), assuming exchange coupled pairs, to $g^{\perp} = 2.27$ and $g^{\parallel} = 2.08$, in agreement with the experimental values. The exchange narrowing of the spectrum is caused probably by ferromagnetic spin correlations, as is indicated by the spontaneous magnetization of Cu cyclotetraphosphate below 7.9 K. No long-range order was detected by ESR spectroscopy. Ferromagnetic long-range order would have led to further drastic changes of the g-values, and antiferromagnetic long-range order would have caused the disappearance of the spectrum. Due to the improved preparation of copper cyclotetraphosphate the presence of impurities can be ruled out and the spontaneous magnetization can no longer be assigned to impurities, as was done before (*11*).

2.2. Manganese cyclotetraphosphate. The ESR spectrum of $Mn_2P_4O_{12}$ exhibits a single symmetric line with the differential

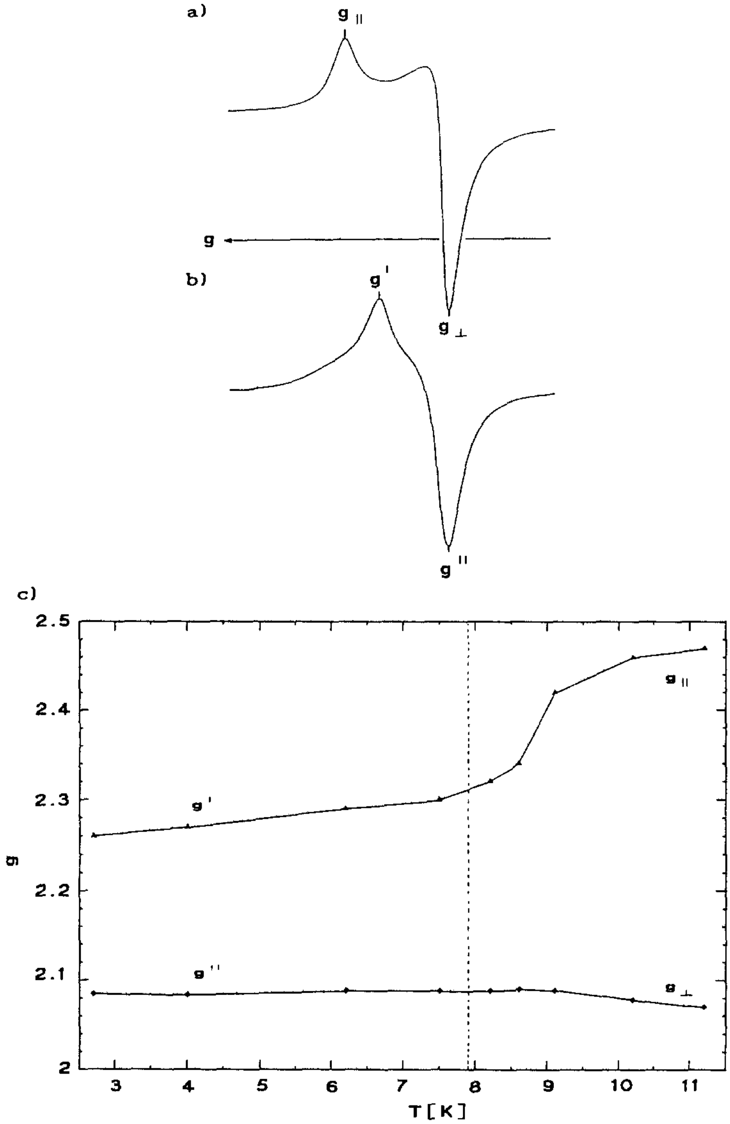

FIG. 6. (a–c) ESR spectra of $Cu_2P_4O_{12}$ (a) at 297 K; (b) at 2.1 K; (c) variation of the g-value with temperature below 11 K. The dotted line at 7.9 K marks the onset of the spontaneous magnetization at zero field.

line width $\Delta B_{\text{diff}} = 0.374(10)$ T and $g = 2.005(6)$. The line shape is Lorentzian. These results differ considerably from those previously reported by Dumante *et al.* (*24*), who found $\Delta B_{\text{diff}} = 0.18$ T and a non-Lorentzian line shape.

The Lorentzian line shape is indicating the presence of exchange interactions. The g-value does not differ much from that of the free electron g_0, as is expected for an ion with an ^6S ground state. Below 100 K the differential line width ΔB_{diff} increases slowly with decreasing temperature (*18*).

Conclusion

Neutron diffraction revealed an overall antiferromagnetic ordering in the cyclotetraphosphates $M_2P_4O_{12}$ with M = Mn, Co, and Ni. No transition to LRO was detected in the Cu compound down to 1.7 K. The magnetic properties of these compounds are certainly determined by interactions of M^{2+} ions located on zigzag chains; however, they do not correspond to simple 1D model systems. The first reason for this discrepancy is the existence of two nonequivalent crystallographic lattice sites, M_{I} and M_{II}, with different crystal field splitting of the cation ground state. This gives rise to unequal magnetic moments. The most pronounced difference was found in the Co compound, where the axial distortion of the local environment of M_{I} and M_{II} sites significantly influences the crystal field splitting of the ^4F free ion ground state. In the Ni compound the crystal field splitting leads to a much weaker anisotropy, and in $Mn_2P_4O_{12}$ it is only a second-order effect. Therefore, the difference in moments, m_{I} and m_{II}, is much smaller for both compounds. A second reason is the fact that certainly more than one intrachain couplings are effective.

Only in the case of $Mn_2P_4O_{12}$, the magnetic properties follow closely the prediction of a 1D Heisenberg model. Antiferromagnetic superexchange couplings via the oxygen bridges are observed, in agreement with the predictions of Anderson (*25*), Slater (*26*), Goodenough (*27*), and Kanamori (*28*). The arrangement of magnetic moments in the Ni and Co compounds implies a ferromagnetic coupling between next-nearest neighbors within the chains. However, the observed spin canting and the two-step metamagnetic behavior of the Co compound indicate strong competition between various inter- and intrachain interactions, giving rise to important frustration effects.

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