

EPR AND IR INVESTIGATIONS OF SOME CHROMIUM (III) PHOSPHATE (V) COMPOUNDS

H. Fuks¹, S.M. Kaczmarek¹ and M.Bosacka²

¹West Pomeranian University of Technology, Institute of Physics, Al Piastów 48, 70-311 Szczecin, Poland

²West Pomeranian University of Technology, Department of Inorganic and Analytical Chemistry; Al. Piastów 42; 71-065 Szczecin, Poland

Received: December 10, 2009

Abstract. A group of four chromium phosphate compounds: $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, $\text{Cr}_2\text{P}_4\text{O}_{13}$ and $\beta\text{-CrPO}_4$ was investigated using the IR and EPR techniques. The Infra-Red spectra allowed us to distinguish two specific vibration bands: a band corresponding to a stretching vibration of the P-O bond (ca. $1400 \div 700 \text{ cm}^{-1}$) as well as a band corresponding to the bending vibrations of the O-P-O groups and vibrations of the Cr-O bonds (ca. $700 \div 300 \text{ cm}^{-1}$). Despite a low crystallographic symmetry (a monoclinic space group), the $\text{Cr}_2\text{P}_4\text{O}_{13}$ phosphate possessed some structural symmetry elements which simplified the IR spectrum.

The EPR results showed the Cr^{3+} ions could not be treated as isolated magnetic ions. In case of all the analyzed samples, trivalent chromium ions created antiferromagnetic exchange coupled pairs or greater antiferromagnetic clusters. The strength of the antiferromagnetic interaction between the species was strongly dependent on the neighboring ions. It seems that PO_4 tetrahedra play a role of mediators in exchange interactions (superexchange).

1. INTRODUCTION

Owing to their interesting properties, phosphates (V) of transition metals, can find many practical applications, e.g., as catalysts, anticorrosive pigments, sensors or materials used in the manufacture of lasers [1-4].

Four chromium (III) phosphates(V): $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, $\text{Cr}_2\text{P}_4\text{O}_{13}$ and $\beta\text{-CrPO}_4$ were synthesized as a result of a solid-state reaction between Cr_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ [5]. The crystal structures of $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_2\text{P}_4\text{O}_{13}$ and $\beta\text{-CrPO}_4$ are well known [6-10]. For our samples they were confirmed by the XRD powder diffraction method.

$\beta\text{-CrPO}_4$ crystallizes in the orthorhombic system with the Cmcm space group, its cell parameters are: $a=0.5165 \text{ nm}$, $b=0.7750 \text{ nm}$, $c=0.6131$, $Z=4$ [6]. The $\beta\text{-CrPO}_4$ structure consists of infinite chains of *trans* edge-sharing CrO_6 octahedra, which run parallel to the *c*-axis. These chains are linked

together by PO_4 tetrahedra. The metal atoms are in the following positions: Cr (4a) and P (4c). [7].

Both $\text{Cr}(\text{PO}_3)_3$ and $\text{Cr}_2\text{P}_4\text{O}_{13}$ crystallize in a monoclinic system [8,9]. The cell parameters of $\text{Cr}(\text{PO}_3)_3$ are: $a = 1.306 \text{ nm}$, $b = 1.8977 \text{ nm}$, $c = 0.9347 \text{ nm}$, $\beta = 127,004^\circ$ with a Cc space group, $Z = 12$ [8]. The structure of $\text{Cr}(\text{PO}_3)_3$ is characterized by one-dimensional infinite metaphosphate chains of PO_4 tetrahedra and isolated CrO_6 octahedra [8, 10]. $\text{Cr}_2\text{P}_4\text{O}_{13}$ crystallizes in a $\text{P}2_1/\text{c}$ space group with $a=0.8097 \text{ nm}$, $b=0.8787 \text{ nm}$, $c=1.3098 \text{ nm}$, $Z=4$ [9]. Hexagonal tunnels along *a*-axis are formed by the edges of two CrO_6 octahedra and four PO_4 tetrahedra. The structure consists of pairs of edge-sharing CrO_6 octahedra forming Cr_2O_{10} units and unusual tetrapolyphosphate anions $\text{P}_4\text{O}_{13}^{6-}$ [9].

Little information about $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ can be found in the available literature [5,11]. Remy *et al.* [11] suggested that $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ was isomorphic with

Corresponding author: S. Kaczmarek, e-mail: skaczmarek@zut.edu.pl

$\text{Fe}_4(\text{P}_2\text{O}_7)_3$ [12]. Much later, Schlesinger *et al.* [13] indexed the diffraction pattern of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$. The cell parameters of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ were found to be: $a = 0.938$ nm, $b = 2.100$ nm, and $c = 0.726$ nm.

The edge sharing CrO_6 octahedra and PO_4 tetrahedra are characteristic features of the analyzed structures, determining also the magnetic properties of chromium phosphates. In this paper a study of the IR and EPR properties of the above mentioned four chromium(III) phosphates(V): $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, $\text{Cr}_2\text{P}_4\text{O}_{13}$, and b-CrPO_4 obtained by solid-state reactions is presented.

2. EXPERIMENTAL

All samples were prepared from Cr_2O_3 , p.a. (Aldrich, Germany) and $(\text{NH}_4)_2\text{HPO}_4$, pure (POCh, Poland) by the conventional calcinations method, according to [5].

The IR spectra of the samples were recorded in the wavenumber range of $1100\div 250$ cm^{-1} by means of a SPECORD M 80 (Carl Zeiss, Jena, Germany) spectrometer.

The purity of the received phases was verified by DTA. The DTA investigations were carried out by means of SDT 2960 (TA Instruments) apparatus. All measurements were conducted in a helium atmosphere. The mass of the samples was as high as ca. 6 mg. They were placed in quartz crucibles. The heating rate was established as $10^\circ/\text{min}$.

The EPR spectra were recorded using a Bruker E 500 X-band spectrometer (~ 9.4 GHz) with a 100 kHz field modulation equipped with an Oxford flow cryostat for measurements in the temperature range of $4\div 300$ K, whereas the magnetic field operated in the range of $10\div 1400$ mT.

3. IR RESULTS

Fig. 1 presents the IR spectra of the all investigated chromium phosphates. The IR spectrum of the new chromium(III) phosphate $\text{Cr}_2\text{P}_4\text{O}_{13}$ is generally in accordance with the spectra of simple chromium(III) phosphates: $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ and CrPO_4 . Two main ranges can be distinguished in the spectra of the four above-mentioned phosphates: a range corresponding to a stretching vibration of the P-O bond (ca. $1400\div 700$ cm^{-1}) as well as a range corresponding to the bending vibrations of the O-P-O groups and vibrations of the Cr-O bonds (ca. $700\div 300$ cm^{-1}) [14,15].

The 1280, 1256, and 1212 cm^{-1} bands observed in the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ can be ascribed to asymmetric stretching vibrations of the P-O bonds

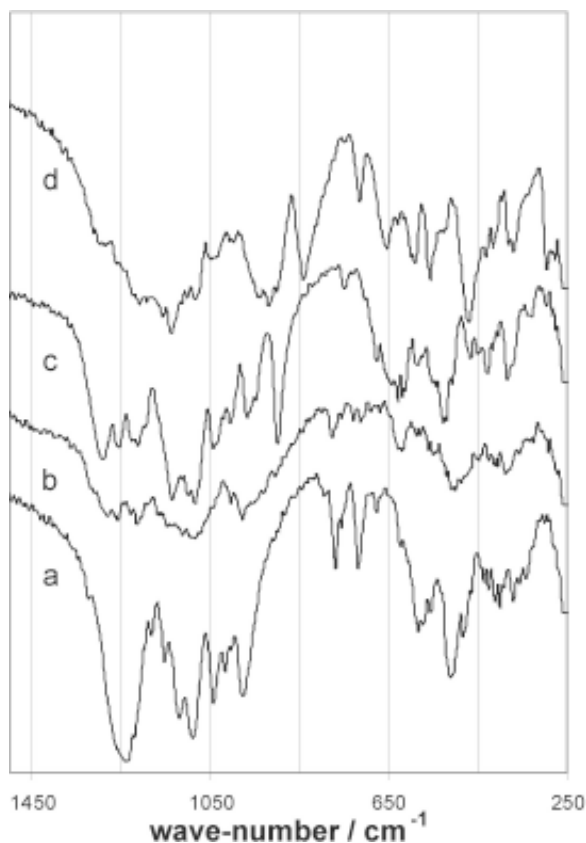


Fig. 1. IR spectrum of : (a) $\text{Cr}(\text{PO}_3)_3$, (b) $\text{Cr}_2\text{P}_4\text{O}_{13}$, (c) $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, and (d) CrPO_4 .

with an external oxygen atom within the PO_2 group. Analogous bands observed in the IR spectrum of $\text{Cr}(\text{PO}_3)_3$: 1236, 1152, 1120, 1088, and 1044 cm^{-1} , are much stronger and more diverse. The bands of variable intensity observed in the $1152\div 1044$ cm^{-1} range are also due to P-O vibrations but showing mixed symmetric-antisymmetric properties. The bands corresponding to PO_2 groups are absent in the IR spectra of two other chromium(III) phosphates, i.e., CrPO_4 and $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ [11,15-19].

The 1084, 1004, and 976 cm^{-1} bands observed in the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ may be due to asymmetric stretching vibrations of the P-O bonds with an external oxygen atom within the PO_3 group. The corresponding bands observed in the IR spectra of CrPO_4 for: 1284, 1208, 1136, 1084, 1048, 944, and 920 cm^{-1} and $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ for: 1288, 1256, 1212, 1136, 1084, 1044, and 1004 cm^{-1} are stronger but generally similar in shape [7, 9, 11, 15-19].

A weak band registered at 776 cm^{-1} occurring in the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ is probably due to symmetric stretching vibrations of the P-O bonds with

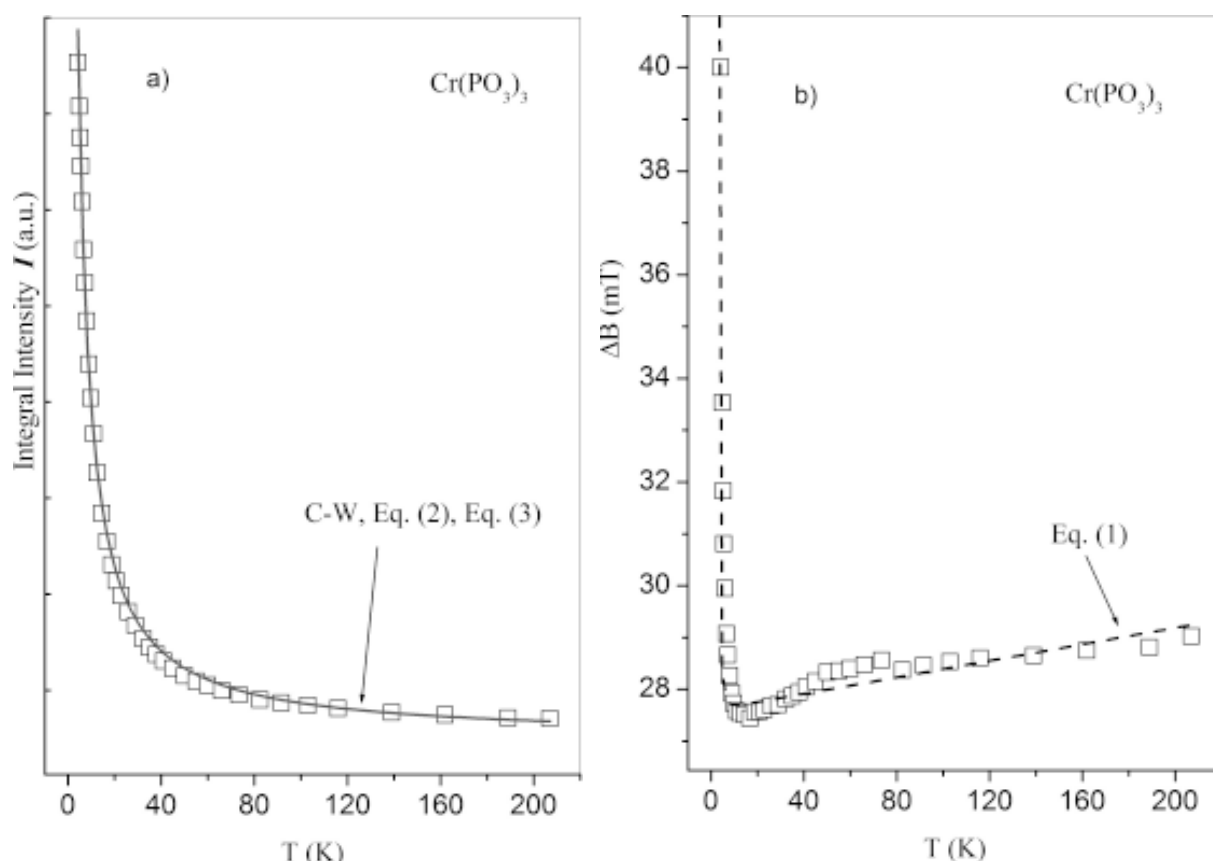


Fig. 2. $I(T)$ and $\Delta B(T)$ relation for $\text{Cr}(\text{PO}_3)_3$ compound. The solid lines represent the results obtained using specific fitting models.

an internal oxygen atom. These vibrations reflect at 720 cm^{-1} in the IR spectrum of $\text{Cr}(\text{PO}_3)_3$ and at 745 cm^{-1} in the IR spectrum of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$. In the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ it is difficult to find any distinct, separate band related to asymmetric stretching vibrations of the P-O bonds with an internal oxygen atom. Such bands can be found at 976 and 768 cm^{-1} in the IR spectrum of $\text{Cr}(\text{PO}_3)_3$, and at 968 and 900 cm^{-1} in the $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ spectrum [11, 15-19].

According to Fig. 1, it is possible to distinguish three different bands in the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ that are covered by a range of lower wave-numbers: 620 and 500 cm^{-1} bands due to asymmetric bending vibrations of the O-P-O groups, and, to stretching vibrations of the Cr-O bonds, as well as a weak band at 388 cm^{-1} due to symmetric bending vibrations of the O-P-O groups or to deformation vibrations of the Cr-O linkage. The first two bands correspond to a more complex and better resolved region in the IR spectra of other phosphates: 584 , 556 , 512 , and 484 cm^{-1} for $\text{Cr}(\text{PO}_3)_3$, 672 , 628 , 620 , and 528 cm^{-1} for $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ and 716 , 652 , 592 , and 556 cm^{-1} for CrPO_4 .

The latter band of the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ is adequate to the 400 and 356 cm^{-1} bands observed in the case of $\text{Cr}(\text{PO}_3)_3$ and to the 428 and 384 cm^{-1} bands observed for $\text{Cr}_4(\text{P}_2\text{O}_7)_3$. Analogous bands: 468 , 416 , 372 , and 296 cm^{-1} are more distinct and intense in the IR spectrum of CrPO_4 [11, 15-20].

A comparatively lower complexity of the IR spectrum of $\text{Cr}_2\text{P}_4\text{O}_{13}$ may be explained by quite small differences between the mean value of the P-O bond length and most of the actual P-O bond lengths. Furthermore, the O-P-O angles with the terminal oxygen atoms deviate from the ideal tetrahedral angle only by a few percent. Thus, despite a low crystallographic symmetry (a monoclinic space group), the $\text{Cr}_2\text{P}_4\text{O}_{13}$ phosphate possesses some structural symmetry elements which simplify the IR spectrum [7, 9, 11, 14-19].

4. EPR RESULTS

A group of chromium phosphate compounds: $\text{Cr}(\text{PO}_3)_3$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, $\text{Cr}_2\text{P}_4\text{O}_{13}$, and $\beta\text{-CrPO}_4$ was investigated using an X-band EPR spectrometer at

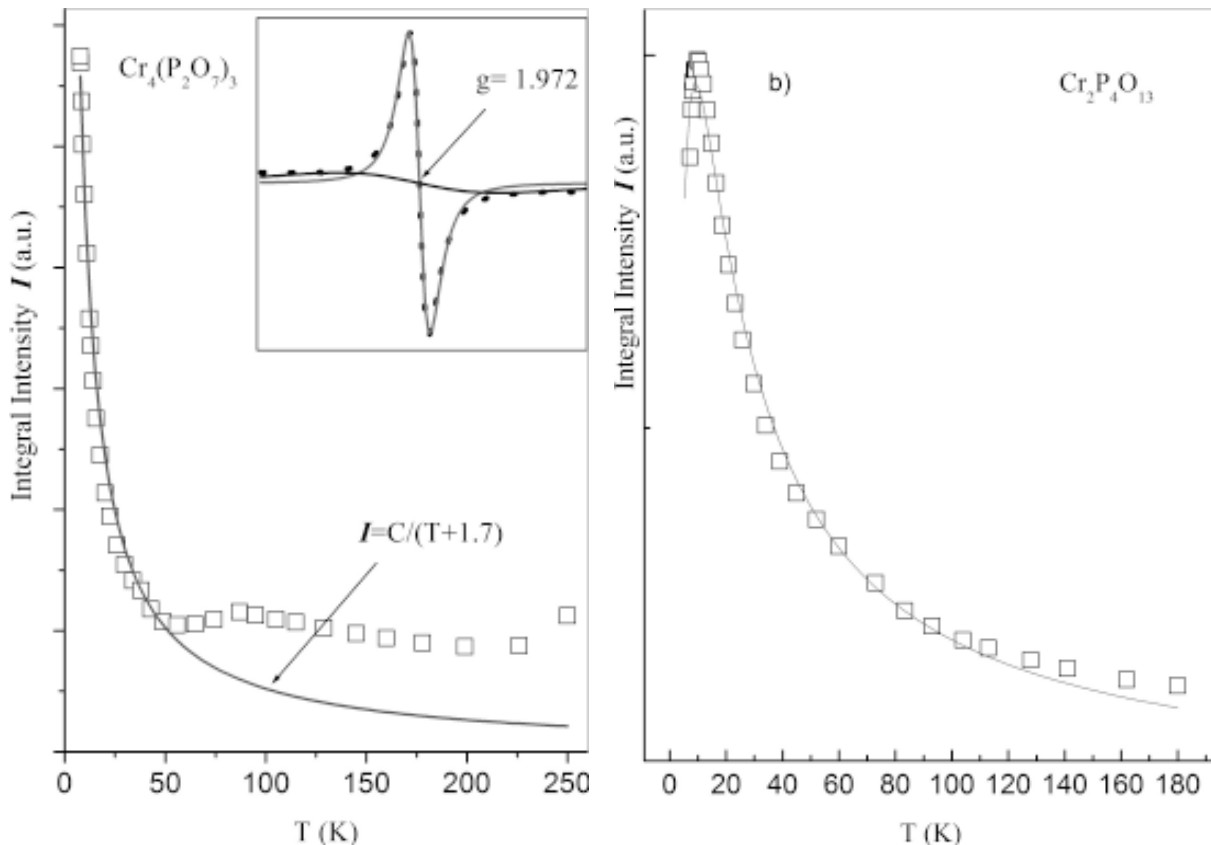


Fig. 3. $I(T)$ relation for $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ (a) and $\text{Cr}_2\text{P}_4\text{O}_{13}$ (b) compounds. The solid line in (a) is the C-W relation and in (b) it represents the simulation result according to Eqs. (2) and (3). The inset in Fig. 3a shows that the EPR signal of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ (dotted line) is a superposition of two Lorentzian lines.

the 4–250K temperature range. A single, narrow and intense EPR line, centered at about 340 mT ($g_{\text{eff}} \approx 1.972$) was observed for all the analyzed samples in whole temperature range. According to the widely known reports [20,21], the isolated trivalent chromium ions give usually a strongly anisotropic EPR resonance signal with the effective value of spectroscopic factors, $g_{\parallel} \sim 5$ and $g_{\perp} \sim 1.9$. A single Lorentzian line observed at a higher resonance field ($g \sim 1.97$) is usually ascribed to the more complex magnetic species, i.e. Cr^{3+} - Cr^{3+} exchange coupled pairs or clusters.

Fig. 2a shows the integral intensity of the EPR signal as a function of temperature for the $\text{Cr}(\text{PO}_3)_3$ compound. In the presented temperature range the integral intensity of EPR signal could be well described by the Curie-Weiss law $I = C/(T - \theta)$, even if the analyzed EPR signal originates from pairs or clusters. The characteristic temperature parameter had small negative value $\theta = -0.8\text{K}$, indicating weak antiferromagnetic (AFM) interactions arising between Cr^{3+} ions. This result seems to be consistent

with some previous reports concerning the magnetic properties of trivalent chromium ions in some phosphates. Rojo et al. [10], for example, have described the magnetic susceptibility in a $\text{Cr}(\text{PO}_3)_3$ compound at temperatures above 5K using the C-W relation. They found that the magnetic susceptibility below 4K was becoming lower and lower due to the beginning of AFM ordering at this temperature. The strength of the AFM interaction was estimated to be as high as $J/k \approx 0.3\text{K}$, whereas the temperature parameter $\theta = -2.7\text{K}$.

In our experiment we could not reach the ordering temperature and directly confirm the complex nature of the chromium magnetic centers. However, the peak-to-peak linewidth as a function of temperature, shown in Fig. 2b, revealed a linear increase in the ΔB values at higher temperatures, unusual for isolated magnetic centers. This behavior suggests that magnetic centers in $\text{Cr}(\text{PO}_3)_3$ may have a rather complex nature, and, an linear increase in the linewidth may be a result of an interaction between spins which is possible via the charge carriers [22].

The collective behavior of the spin system leads to a spin frustration and changes the spin lattice relaxation rate. In case of an antiferromagnetically coupled system, the $\Delta B(T)$ function could be described by the modified Huber equation:

$$\Delta B(T) = a \left(\frac{T - T_N}{T_N} \right)^b + cT + \Delta B_0, \quad (1)$$

where: T_N - Neel temperature, b - critical exponent, c - slope of linear dependence, ΔB_0 - residual linewidth. As could be seen from Fig. 2b, the fitting performed using Eq. (1) with the parameters: $T_N = 1.4\text{K}$, $b = -3.6$, $c = 0.008\text{ mT/K}$ and $\Delta B_0 = 27.6\text{ mT}$ is quite good. The calculated parameters are similar to those reported in [22] where the complex nature of the Cr^{3+} system has been concluded, too. However, the obtained Neel temperature, $T_N = 1.4\text{K}$, is not exactly comparable with the ordering temperature $\sim 4\text{K}$, reported in [10] which suggests the necessity to make a correction of the model represented by Eq. (1).

The calculation of the relative intensity of the EPR line for Cr^{3+} - Cr^{3+} pairs has been given by Fournier *et al.* [23]. Generally, the value of sample magnetic susceptibility for metallic d^3 - d^3 ions, being proportional to the EPR signal integral intensity can be described by the following equation [24]:

$$\chi(T) = \frac{C(2e^{-5J/T} + 10e^{-3J/T} + 28)}{T(e^{-6J/T} + 5e^{-3J/T} + 3e^{-5J/T} + 7)}, \quad (2)$$

where: J - is the exchange coupling parameter [K].

In case of a more complex magnetic system where the exchange coupling creates AFM clusters, a description of the integral intensity could be done by the following equation [25]:

$$I(T) = c / T e^{-E/T}, \quad (3)$$

where: E - is energy between the ground (nonmagnetic) state and the first excited state of the AFM cluster [K].

The experimental points shown in Fig. 2a were confronted with both models and no clear answer which model was better for the $\text{Cr}(\text{PO}_3)_3$ compound was obtained. The fitting performed using a dimeric model (Eq. (2)) gives the exchange energy, $J = -0.55\text{K}$, whereas the cluster model (Eq. (3)) gives parameter $E = 0.76\text{K}$. It can be concluded from both models that trivalent chromium ions arise in a complex magnetic arrangement with a low AFM ordering temperature in this compound.

Fig. 3a shows the integral intensity of the EPR signal as a function of temperature for the $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ compound. As can be seen the experimental points deviate from the C-W relation (solid line) indicating the existence of at least two different chromium magnetic centers: one with the ordering temperature of $\sim 80\text{K}$ and the other with the ordering temperature of $T_N < 4\text{K}$. The inset in Fig. 3a shows that the EPR signal is not a single Lorentzian line but could be represented by two lines of a different width. The overall linewidth of the EPR signal registered for this sample revealed no significant temperature changes ($\Delta B \sim 30\text{ mT}$), partly due to the mutual overlapping of more than one resonance lines.

The constant linewidth value ($\Delta B \sim 40\text{ mT}$) is a common feature of another $\text{Cr}_2\text{P}_4\text{O}_{13}$ compound. Fig. 3b shows the integral intensity of the EPR signal as a function of temperature. It can be seen that the intensity increases with the decreasing temperature according to the Curie-Weiss law, reaching a maximum at 10K . Below this temperature the intensity significantly drops indicating the AFM ordering of the chromium magnetic centers. The fitting of the $I(T)$ relation using Eq. (2) and 3 gives $J = -5.4\text{K}$ and $E = 9\text{K}$, respectively. It follows from the above that the $\text{Cr}_2\text{P}_4\text{O}_{13}$ compound reveals significantly stronger AFM exchange coupling, comparing to $\text{Cr}(\text{PO}_3)_3$.

Fig. 4a shows the integral intensity of the EPR signal as a function of temperature for the $\beta\text{-CrPO}_4$ compound. Above 50K the integral intensity follows the C-W law with a very high negative value $\theta = -250\text{K}$, indicating strong AFM interactions between chromium ions. At low temperatures, $I(T)$ deviates from the C-W model, and the magnetic centers approach the AFM ordering starting at temperatures below 30K .

The peak-to-peak linewidth as a function of temperature, shown in Fig. 4b, reveals a significant decrease with the increasing temperature which indicates a quite different relaxation mechanism in the spin system with respect to the previously analyzed chromium phosphates.

5. CONCLUSIONS

A group of four chromium (III) phosphates (V) was analyzed by the IR and EPR methods. The structure of the presented compounds is very well known with the characteristic mutual occurrence of CrO_6 octahedra and PO_4 tetrahedra.

The EPR results showed that Cr^{3+} ions could not be treated as isolated magnetic ions. In case of all the analyzed samples it was found that trivalent

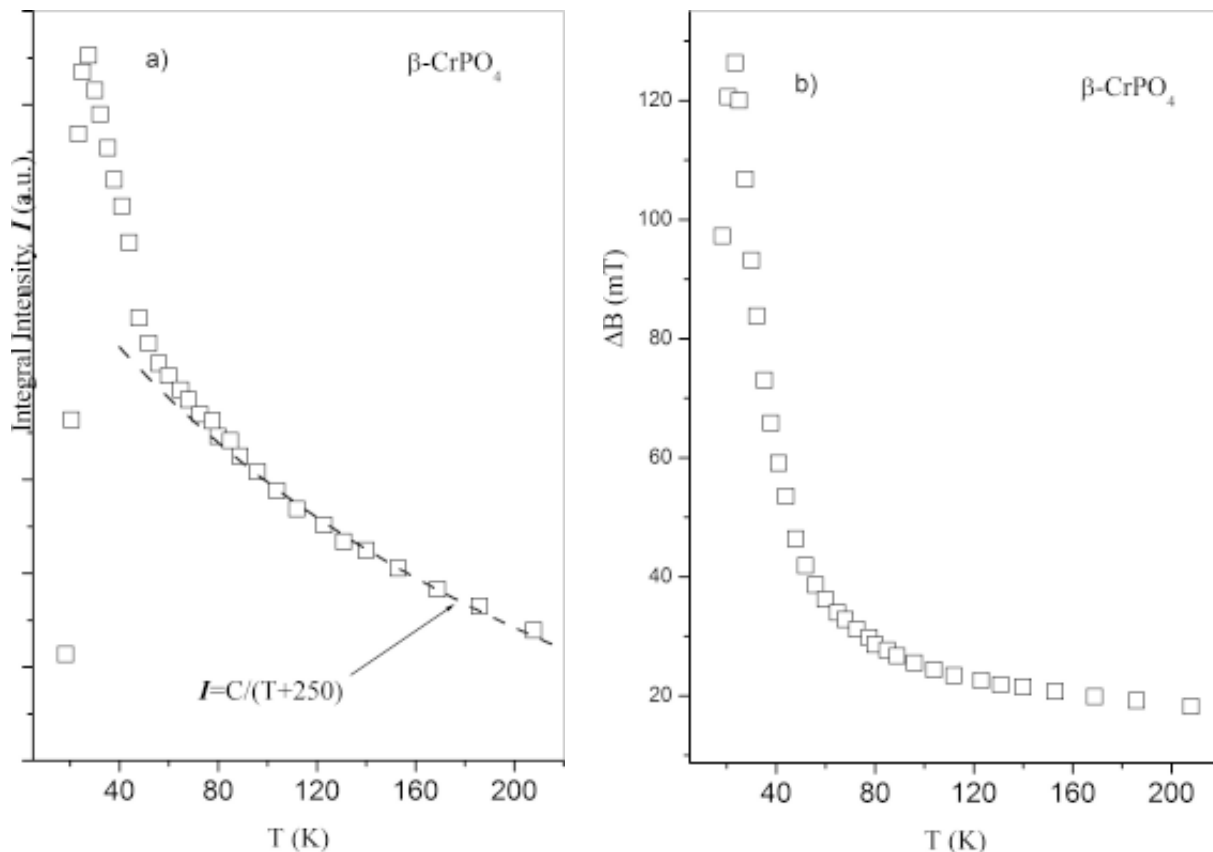


Fig. 4. $I(T)$ and $\Delta B(T)$ relation for $\beta\text{-CrPO}_4$ compound. The dashed line is the C-W relation.

chromium ions created antiferromagnetic exchange coupled pairs or a greater, complex network forming AFM clusters. The strength of the AFM interaction was strongly dependent on the neighboring ions. It seems that PO_4 tetrahedra play the role of mediators of specific exchange interactions (superexchange).

The superexchange interactions were weak and the ordering temperature, T_N , was very low particularly in $\text{Cr}(\text{PO}_3)_3$ where CrO_6 octahedra were well isolated from the PO_4 tetrahedral system. A weak exchange interaction enabled us to detect other magnetic interactions, i.e., between magnetic spins and lattice carriers, observed in the $\Delta B(T)$ function as a linear increase in ΔB with temperature. The calculated Neel temperature, $T_N = 1.4\text{K}$, was significantly different than $T_N \sim 4\text{K}$ obtained from direct measurements of magnetic susceptibility [10] which suggested that a paired model was not proper in this case, and that a more complex magnetic network should be responsible for this signal.

Contrary to $\text{Cr}(\text{PO}_3)_3$, the chromium octahedra in $\text{Cr}_2\text{P}_4\text{O}_{13}$ compound were clearly edge shared with phosphate tetrahedra. As a result, the exchange interaction was much stronger and the AFM ordering began just below 10K. Due to a strong exchange it was possible to maintain a constant value of the EPR linewidth.

A similar situation was observed in the $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ compound, however two different magnetic centers were revealed in the latter case. The knowledge about the exact structure of this material is not clear to date.

The EPR results registered for the $\beta\text{-CrPO}_4$ compound indicated the existence of very strongly AFM coupled chromium magnetic centers. The integral intensity did not fit well with the lines calculated from a dimer model relation (Eq. (2)) or a simple cluster model (Eq. (3)). This discrepancy was attributed to specific connections between CrO_6 octahedra and PO_4 tetrahedra, creating a spiral of magnetic moments in a plane perpendicular to the chains of *trans* edge-sharing CrO_6 octahedra in $\beta\text{-CrPO}_4$.

REFERENCES

- [1] L. Lezama, J.M. Rojo, J.L. Mesa, T. Rojo and R. Olazcuaga // *J. Solid State Chem.* **115** (1995) 146.
- [2] G.S. Gopalakrishna, M.J. Mahesh and K.G. Ashamanjari // *J. Crystal Growth* **284** (2005) 495.
- [3] Kirk Othmer, *Encyklopedie of Chemical Technology*, vol. 18, (Wiley, 1996).
- [4] R. Bojko, V. Boyko, O. Gomenyuk, P. Nagorniy, S. Nedilko, I. Nedyelko and N. Stus // *Opt. Mater.* **30** (2008) 693.
- [5] M. Bosacka, P. Jakubus and I. Rychlowska-Himmel // *J. Therm. Anal. Cal.* **88** (2007) 133.
- [6] E.J. Baran // *J. Mater. Sci.* **33** (1998) 2479.
- [7] J.P. Attfield, P.D. Battle, A.K. Cheetham and D.C. Johnson // *Inorg. Chem.* **28**(1989) 1207.
- [8] M. Gruss and R. Glaum // *Acta Cryst.* **C52** (1996) 2647.
- [9] K.H. Lii, Y.B. Chen, C.C. Su and S.L. Wang // *J. Solid State Chem.* **82** (1989)156.
- [10] J.M. Rojo, J.L. Mesa, L. Lezama and T.Rojo // *J. Mater.Chem.* **7** (1997) 2243
- [11] P. Remy and A. Boulle // *Bull. Soc. Chim. France* **6** (1972) 2213.
- [12] L. K. Elbouaanani, B. Malaman, R. Gehrardin and M. Ijjaali // *J. Sol. St. Chem.* **163** (2002) 412
- [13] K.von Schlesinger, B. Ziemer, W.Hanke and G.Ladwig // *Z. Anorg. Allg. Chem.* **500** (1983) 104.
- [14] A. Rulmont, R. Cahay, M. Liegeois-Duyckaerts and P. Tarte // *Eur. J. Solid State Inorg. Chem.* **28** (1991) 207.
- [15] L. Lezama, J.M. Rojo, J.L. Pizarro, M.I. Arriortua and T. Rojo // *Solid State Ionic* **63-65** (1993) 657.
- [16] E.J. Baran and D.I. Roncaglia // *Spectrochim. Acta A* **44** (1988) 399.
- [17] J.P. Attfield and A.K. Cheetham // *J. Appl. Cryst.* **21** (1988) 252.
- [18] A. Bielański, J. Pozniaczek and E. Wenda // *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **6** (1976)485.
- [19] D. Olivier // *Rev. Chim. Miner.* **6** (1967) 1066.
- [20] I. Ardelean, M. Peteanu, V. Simon, C. Bob and S. Filip // *J. Mater. Sci.* **33** (1998) 357.
- [21] R.P. Sreekanth Chakradhar, A. Murali and J.L. Rao // *J. All. Comp.* **281** (1998) 99.
- [22] A. Worsztynowicz, S.M. Kaczmarek, M. Kurzawa and M. Bosacka // *J. Solid State Chem.* **178** (2005) 2231.
- [23] J.T. Fournier, R.J. Landry and R.H. Bartram // *J. Chem. Phys.* **55** (1971) 2522.
- [24] B. Jezowska-Trzebiatowska and W. Wojciechowski // *Trans. Metal. Chem.* **6** (1970) 1.
- [25] J. Yoshikawa, C. Urakawa, H. Ohta, T. Koide, T. Kawamoto, Y. Fujiwara and Y. Takeda // *Physica E* **10** (2001) 395.