

Electronic Spectra of (Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> PhasesEnrique J. Baran,<sup>a</sup> Anders G. Nord,<sup>b,\*</sup> Ekkehard Diemann<sup>c</sup> and Tore Ericsson<sup>d</sup><sup>a</sup>Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900-La Plata, Argentina, <sup>b</sup>Department of Structural Chemistry, Arrhenius Laboratory, S-10691 Stockholm, Sweden, <sup>c</sup>Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld, F.R.G. and <sup>d</sup>Department of Mineralogy and Petrology, Institute of Geology, University of Uppsala, Box 555, S-751 22 Uppsala, SwedenBaran, J.E., Nord, A.G., Diemann, E. and Ericsson, T., 1990. Electronic Spectra of (Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> Phases. – Acta Chem. Scand. 44: 513–515.

As a continuation of a series of studies on the spectroscopic properties of different oxosalts and to obtain a wider insight into the electronic characteristics of metal–oxygen chromophores, we have now investigated the electronic spectra of a series of solid solutions of the type (Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, isostructural with α-Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

The crystal structure of α-Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> was determined in 1967 by Calvo.<sup>1</sup> Later Krishnamachari and Calvo have shown that α-Co<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is isostructural with α-Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.<sup>2</sup> The monoclinic space group symmetry is B2<sub>1</sub>/c (No. 14), with one distinct five- and one six-coordinated metal site (Z=8). The average metal–oxygen distances are 2.044 Å (five-coordination; range 1.985–2.120) and 2.103 Å (six-coordination; range 2.059–2.142) in α-Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>,<sup>1</sup> and 2.049 (1.957–2.110) and 2.116 Å (2.062–2.183), respectively, in α-Co<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.<sup>2</sup> The MO<sub>6</sub> groups are fairly regular octahedra, while the MO<sub>5</sub> polyhedra should rather be described as square pyramids.

## Experimental

Pure diphosphates of magnesium and cobalt (II) and four α-(Mg<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> solid solutions (x = 0.2, 0.4, 0.6 and 0.8) were prepared as described earlier.<sup>3</sup> X-Ray powder

diffraction data were obtained with a Guinier-Hägg camera (Cr Kα<sub>1</sub> radiation, λ = 2.28975 Å, R = 50.00 mm, KCl internal standard) and evaluated with the computer program system by Nord and Forsberg<sup>4</sup> to give the unit-cell dimensions presented in Table 1. The figures of merit are according to de Wolff.<sup>5</sup> The electronic reflectance spectra were recorded with a Beckman ACTA-IV instrument between 250 and 870 nm, with an integrating sphere employing TiO<sub>2</sub> as a standard.

## Results and discussion

The reflectance spectra of the (Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phases are similar to each other (Fig.1). A larger cobalt content implies more CoO<sub>n</sub> chromophores and also a better defined spectrum. Spectra of phases with lower cobalt contents show some broadening of the bands at 21.5 × 10<sup>3</sup> and 19.23 × 10<sup>3</sup> cm<sup>-1</sup>, but the transition energies do not change significantly with the composition.

Two different chromophoric groups are present in this structure, and the observed transitions must therefore be related to the CoO<sub>6</sub> and CoO<sub>5</sub> groups. For the octahedral CoO<sub>6</sub> chromophore two electronic bands are expected in the measured range<sup>6</sup> and have been assigned to the strong

Table 1. Unit-cell dimensions for the α-(Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> diphosphates.

Phase <sup>a</sup>	a/Å	b/Å	c/Å	β/°	V/Å <sup>3</sup>	N <sup>b</sup>	M(20) <sup>c</sup>
Mg <sub>100</sub>	13.240(4)	8.291(2)	9.050(3)	104.65(3)	961.2(6)	38	103
Mg <sub>80</sub> Co <sub>20</sub>	13.242(5)	8.298(4)	9.038(4)	104.57(5)	961.2(9)	32	89
Mg <sub>60</sub> Co <sub>40</sub>	13.253(6)	8.306(5)	9.032(5)	104.59(6)	962.2(11)	28	76
Mg <sub>40</sub> Co <sub>60</sub>	13.252(7)	8.322(5)	9.020(5)	104.59(7)	962.7(14)	25	58
Mg <sub>20</sub> Co <sub>80</sub>	13.248(9)	8.327(7)	9.014(8)	104.62(9)	962.2(16)	22	43
Co <sub>100</sub>	13.249(3)	8.341(2)	9.003(2)	104.64(2)	962.6(6)	36	93

<sup>a</sup>Mg<sub>100</sub> stands for pure α-Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, Mg<sub>80</sub>Co<sub>20</sub> for α-(Mg<sub>0.80</sub>Co<sub>0.20</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and so forth. <sup>b</sup>N = number of reflections used in the refinements. <sup>c</sup>M(20) = figure of merit according to de Wolff.<sup>5</sup>

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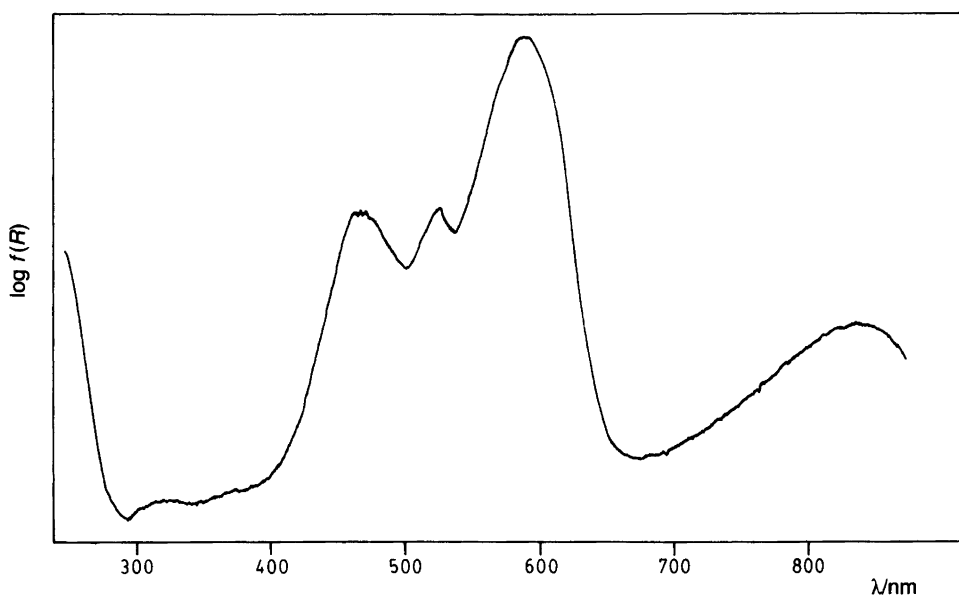


Fig. 1. Spectrum for the solid solution  $\alpha$ -(Mg<sub>0.20</sub>Co<sub>0.80</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (reflectance versus TiO<sub>2</sub>).

bands at 585 nm ( $17.10 \times 10^3 \text{ cm}^{-1}$ ) and 520 nm ( $19.23 \times 10^3 \text{ cm}^{-1}$ ). These are related to the  ${}^4F_{1g} \rightarrow {}^4A_{2g}$  (F) and  ${}^4F_{1g} \rightarrow {}^4F_{1g}$  (P) transitions, respectively. A third band, corresponding to the  ${}^4F_{1g} \rightarrow {}^4F_{2g}$  (F) transition, is expected to lie at around  $8.5 \times 10^3 \text{ cm}^{-1}$  as predicted from the known relation  $\nu_2/\nu_1 \approx 2$  (Ref. 6).

For the assignment of the transitions of the square-pyramidal CoO<sub>5</sub> chromophore ( $C_{4v}$  symmetry) we have used the energy-level diagram proposed by Ciampolini and Bertini,<sup>7</sup> based on the weak-field scheme with F-P term intermixing (cf. Fig. 2 and Ref. 8). According to this scheme, the following band assignments can be proposed:

465 nm ( $21.5 \times 10^3 \text{ cm}^{-1}$ ) to  ${}^4A_2 \rightarrow {}^4A_2$  (P)

585 nm ( $17.1 \times 10^3 \text{ cm}^{-1}$ ) to  ${}^4A_2 \rightarrow {}^4E$  (P)

835 nm ( $12.0 \times 10^3 \text{ cm}^{-1}$ ) to  ${}^4A_2 \rightarrow {}^4B_1$ .

A fourth transition, expected at around  $(7-8) \times 10^3 \text{ cm}^{-1}$  and assignable to the  ${}^4A_2 \rightarrow {}^4E$  transition, lies outside the range of our instrument.

The second transition of the CoO<sub>5</sub> chromophore coincides with the  ${}^4F_{1g} \rightarrow {}^4A_{2g}$  transition of the CoO<sub>6</sub> group. This explains the intensity enhancement observed for this band. In an octahedral environment this band usually has a lower intensity than that corresponding to the  ${}^4F_{1g} \rightarrow {}^4F_{1g}$  (P) transition. Moreover, in square-pyramidal environments this band generally presents an intensity comparable to that of the  ${}^4A_2 \rightarrow {}^4A_2$  (P) transition.<sup>6-8</sup> A similar intensity enhancement has also been found previously in cobalt-containing solid solutions isomorphous with  $\gamma$ -Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, in which octahedral CoO<sub>6</sub> groups and distorted trigonal bipyramids CoO<sub>5</sub> are found together. The last very weak band located at 320 nm ( $31.25 \times 10^3 \text{ cm}^{-1}$ ) can probably be as-

signed to a spin-forbidden transition which involves a level originating from higher doublet terms.<sup>9</sup>

The cation distribution in two (Mg,Co)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> solid solutions has earlier been determined from X-ray diffraction data,<sup>10</sup> showing that there is a slight tendency for Co<sup>2+</sup> to enter preferably the five-coordinated site rather than the six-coordinated site ( $K_D \approx 2$ ). The metal-oxygen distances are comparable to those of the (Mg,Co) diphosphates, but the MO<sub>5</sub> group should rather be described as a distorted trigonal bipyramid. For instance, in (Mg<sub>0.5</sub>Co<sub>0.5</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> the respective average metal-oxygen distances are 2.06 Å

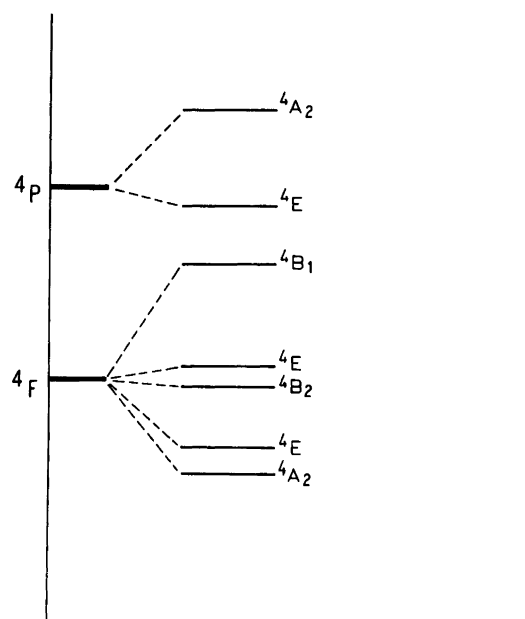


Fig. 2. Schematic splitting of Co(II) free-ion levels in  $C_{4v}$  symmetry.

(five-coordination; range 1.94–2.21) and 2.08 Å (six-coordination; range 2.04–2.11).<sup>10</sup>

A comparison of the electronic spectra recorded earlier for some (Mg,Co) orthophosphates<sup>11</sup> and here reported for four  $\alpha$ -(Mg,Co)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phases suggests that in the latter phases also Co<sup>2+</sup> prefers to enter the five-coordinated site. This is in accordance with Burns' observation that Co<sup>2+</sup> ions are enriched in distorted and small-dimension sites, while magnesium seems to have a greater tendency for octahedral sites.<sup>12</sup> The present results also extend our knowledge in relation to MO<sub>6</sub> and MO<sub>5</sub> chromophores, and show that the spectra of CoO<sub>5</sub> chromophores with a square-pyramidal configuration are, within the resolution of our instrument, very similar to those of trigonal-bipyramidal systems, as is known for some other Co<sup>2+</sup> compounds.<sup>6,7</sup>

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