MAGNETIC BEHAVIOR OF Co^{2+} IONS IN SYNTHETIC MINERALS RELATED TO VIVIANITE AND LUDLAMITE

J. Pizarro, L. Lezama, Gérard Villeneuve, M. Arriortua, T. Rojo

► To cite this version:

J. Pizarro, L. Lezama, Gérard Villeneuve, M. Arriortua, T. Rojo. MAGNETIC BEHAVIOR OF Co^{2+} IONS IN SYNTHETIC MINERALS RELATED TO VIVIANITE AND LUDLAMITE. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-2063-C8-2064. 10.1051/jphyscol:19888935 . jpa-00229213

HAL Id: jpa-00229213

<https://hal.science/jpa-00229213>

Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

MAGNETIC BEHAVIOR OF Co^{2+} IONS IN SYNTHETIC MINERALS RELATED TO VIVIANITE AND LUDLAMITE

J. L. Pizarro ⁽¹⁾, L. Lezama ⁽¹⁾, G. Villeneuve ⁽¹⁾, M. I. Arriortua ⁽²⁾ and T. Rojo ⁽²⁾

⁽¹⁾ Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 33405 Talence, France

⁽²⁾ Facultad de Ciencias, UPV, BILBAO, Spain

Abstract. — Members of the family of mineral vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, and ludlamite $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ involving Co^{2+} ions have been synthesized. $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ exhibits an antiferromagnetic ordering at 6.5 K, the nature of the interactions are discussed with respect to its crystal structure. Using hydrothermal conditions tetra and dihydrate were obtained. The ferrimagnetism observed for the tetrahydrate may be related to the ludlamite structure. A spin-flop is observed for the dihydrate at a critical field of 1 kG.

Introduction

Among the compounds with general formula $\text{A}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ three of them occur in nature as minerals when $\text{A} = \text{Fe}^{II}$: vivianite ($n = 8$), ludlamite ($n = 4$) and phosphoferrite ($n = 3$). These minerals have been synthesized (1) as well as other members of the homologous series corresponding to $n = 2$ and 1. Their crystal structure are favorable to the presence of complex magnetic interactions with — mainly — a low dimensional character.

The magnetic properties of vivianite and ludlamite have been intensively studied by susceptibility, Mössbauer spectroscopy and specific heat measurements [1-6]. It appears that the magnetic behavior of vivianite is rather complicated, involving at least two magnetic systems which, moreover, are not independent of each other [11]. A full 3D ordering occurs below 9 K [2]. The behavior of ludlamite seems to be well understood with respect to its magnetic structure which consists in ferromagnetic Fe^{2+} trimers coupled by an antiferromagnetic intertrimer interaction [5].

Substitution of Fe^{II} by Co^{II} was expected to cause some modifications of this magnetic behavior, due to the large g -factor anisotropy of Co^{2+} in a distorted octahedral environment.

In this article we report the synthesis of hydrates $\text{Co}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 8, 4, 2$) homologous to iron compounds.

Their magnetic properties are presented and discussed with respect to the crystal structure when it is known.

Synthesis and characterization

$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ was obtained from aqueous solution of cobalt sulfate and ammonium phosphate at about 70 °C. This compound was used as a precursor for the synthesis of the tetra and dihydrate using hydrothermal conditions into a sealed gold tube. Working at 160 °C and 350 atm during 5 days we obtain

a violet powder of $\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; increasing the temperature (225 °C) and the pressure (400 atm) small purple crystals of $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are formed as a single phase. These compounds were characterized by X-ray diffraction, thermogravimetry and IR spectroscopy.

Magnetic properties

$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. — The crystal structure of $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is isotype to that of vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ determined by MORI and ITO [7] which is represented in figure 1.

Its magnetic susceptibility follows, at high temperature, a Curie-Weiss law $\chi = C/T - \theta$ with $c = 3.20$ per Co^{2+} and $\theta = -11$ K. The Curie constant value is in good agreement with those generally found for Co^{2+} ions in distorted octahedral site. At low temperature a 3D antiferromagnetic ordering occurs at 6.5 K, due to a complex coupling involving at least four exchange interactions:

- a direct interaction involving d_{xy} orbitals of Co^{2+} in dimeric sites (antiferromagnetic);
- a superexchange intradimer interaction via oxygen involving $d_{x^2-y^2}$ orbitals (ferromagnetic);

Fig. 1. — Crystal structure of vivianite.

- a superexchange interdimer interaction via PO_4 group, $d_{x^2-y^2} - \text{PO}_4 - d_{x^2}$ (antiferromagnetic);
- a superexchange interaction via PO_4 group between cobalt in dimers and monomers, $d_{x^2} - \text{PO}_4 - d_{x^2}$ (antiferromagnetic).

The sign of the different coupling are obtained following Anderson-Goodenough-Kanamori rules [8-10].

$\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. - The structure of the tetrahydrate $\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is unknown. Nevertheless the study of the magnetic susceptibility clearly shows a ferrimagnetic ordering at 4.5 K (Fig. 2). In the homologous mineral ludlamite $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, the magnetic structure consists in ferromagnetic trimers of Fe^{2+} with an antiferromagnetic intertrimers coupling. If we assume that the structure of the cobalt phosphate tetrahydrate is related to that of ludlamite, the observed ferrimagnetism behavior can be explained by the strong anisotropy of the Co^{2+} g-factor, giving rise to uncompensated magnetic moments.

Fig. 2. - Magnetic behavior of $\text{Co}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

$\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. - The magnetization of the dihydrate $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ exhibits a rather complex behavior (Fig. 3). Below 11 K its field dependence shows an anomalous increase between 1 and 10 kG. This indicates a Co^{2+} spin-flop at a critical field $H_c \simeq 1$ kG in the 3D ordered region. The susceptibility was measured at fields lower than 1 kG in order to avoid the

Fig. 3. - Magnetization of $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ as a function of magnetic field at 4.5 K.

effects of the spin flop. At high temperature it follows a Curie-Weiss law with $C = 2.77$ emu per Co^{2+} and $\theta = -42$ K. Considering the behavior of the product χT vs. T (Fig. 4) one can observe three domains.

Fig. 4. - Experimental χT values of $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the 4-250 K range.

Above 18 K, the evolution of χT is typical of low dimensional ferrimagnetic behavior (cluster, 1D ?). Below 11 K a 3D antiferromagnetic ordering occurs. The behavior between 11 and 18 K is not yet clearly understood.

Acknowledgements

We thank the Basque Government/Eusko Jaurlaritz for a doctoral Fellowship to 2 of us (J.L.P. and L.L.).

- [1] Mattievich, E. and Danon, J., *J. Inorg. Nucl. Chem.* **39** (1977) 569-580.
- [2] Meijer, H. C., Van Den Handel, J., Frikkee, E., *Physica* **34** (1967) 475-483.
- [3] Meijer, H. C., Giesen, J. J. and Van Den Handel, J., *Physica* **38** (1968) 227-232.
- [4] Meijer, H. C., Adair, III T. W. and Van Den Handel, J., *Physica* **38** (1968) 233-240.
- [5] Abrahams, S. C., *J. Chem. Phys.* **44** (1966) 2230-2237.
- [6] Forstat, H., Love, N. D., Mac Elearney, J. N. and Butterworth, G. J., *Phys. Rev.* **1** (1970) 3097-3100.
- [7] Mori, H. and Ito, I., *Acta Cryst.* **3** (1950) 1-6.
- [8] Anderson, P. W., *Phys. Rev.* **13** (1958) 1492.
- [9] Goodenough, J. B., *Magnetism and the Chemical bond* (Interscience Publ., New York) 1963.
- [10] Kanamori, J., *Phys. Chem. Solids* **10** (1958) 87.
- [11] Forsyth, J. B., Johnson, C. E., Wilkinson, C., *J. Phys. C: Solid St. Phys.* **3** (1970) 1127-1139.