Crystal structure and magnetism of Co(HPO₃)·H₂O: A novel layered compound of Co(II)

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The crystal structure and magnetic properties of $Co(HPO_3) \cdot H_2O$ have been determined. The solid crystallizes in space group $Pca2_1$, $a = 8.984(2)$ Å, $b = 7.918(2)$ Å, $c = 10.139(8)$ Å, $V = 721.2$ Å^3. $Z = 4$ $d_{calc} = 2.89$ g/cm^3. The structure consists of layers only connected by hydrogen bonds. These layers can be viewed as formed by zigzag chains of edge-sharing $Co(II)O_6$ octahedra interconnected by a three atom bridge (O-P-O) and a single oxygen bridge. ac magnetic susceptibility measurements show a sharp peak at $T_c = (10.8 \pm 0.1)$ K, and are consistent with a transition from one- to two-dimensional magnetic order, in agreement with the structure. An analysis of the $\chi T/C$ vs $\epsilon = (1 - T_c/T)$ data in the critical region, for $T > T_c$, using a double-logarithmic plot, yields a critical exponent $\gamma = 1.75$ for $0.01 < \epsilon < 0.1$, which correspond to a two-dimensional Ising model.

I. INTRODUCTION

Continuing our work on low-dimensional magnetic systems,[1-3] several solid phases based on transition metal phosphates have been structurally and magnetically characterized.[4-6] The chemistry of transition metal derivatives of low-oxidation oxophosphoric acids is complicated by redox reactions and has not been so widely studied.[7,8] On the other hand, the fact the HPO_3^{2-} and $H_2PO_2^-$ contain only three and two donor oxygen atoms, respectively, (as opposed to four in PO_4^{3-}) makes them good candidates to build lower dimensional solids containing transition metals. The present work represents our first report on this kind of solids, and includes the crystal structure and magnetic properties of a new layered phase of empirical formula $Co(HPO_3) \cdot H_2O$. Single crystals of this material have been prepared by hydrothermal treatment of a solution of Co(II), HPO₃H₂, and a base, but can also be obtained from H_2PO_2H.[9]

II. DATA COLLECTION

A red-purple thin plate crystal of $[Co(HPO_3) \cdot H_2O]$ having approximate dimensions of $0.27 \times 0.22 \times 0.02$ mm was used. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 18 reflections in the range $6 < \theta < 15°$. From the systematic absences of $0,k,l$ k odd, $(0,k,0$ k odd), $h,0,l$ l odd, and $(0,0,l$ l odd), the space group was initial considered by the $Pbcm$.

The data were collected at room temperature using the $w/2\theta$ scan technique to a maximum 2θ of 50.0°. A total of 2752 reflections were collected. Lorentz and polarization corrections were initially applied to the data and intensities of equivalent reflections were averaged.

III. STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the Patterson method and was initially refined in space group $Pbcm$. To the Co atom found in the Patterson map, P and O atoms were added after successive difference Fourier syntheses, but that structural model did not refine below an R factor of 0.14. At this point, conversion to space group $Pca2_1$ was accomplished with a concomitant rotation of the crystallographic axes interchanging a and b, and the refinement continued successfully [$a = 8.984(2)$ Å, $b = 7.918(2)$ Å, $c = 10.139(8)$ Å, $V = 721.2$ Å^3. $Z = 4$ $d_{calc} = 2.89$ g/cm^3]. Anisotropic refinement yielded negative temperature factors for several atoms, P1 among them. Then a numerical absorption correction was applied to the original unaveraged data, which were then averaged and used in the least-squares refinements, lowering slightly the R factors and, more importantly, leading to more reasonable anisotropic parameters for all atoms.

All hydrogen atoms were located in difference Fourier syntheses and their positions were refined in least squares; their isotropic thermal parameters were held fixed at values ~20% higher than those atoms to which they are bonded. Only the 907 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements.

The final cycle of refinement included 77 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.036$ $R_w = 0.044$. The standard deviation of an observation of unit weight was 1.195. The final difference Fourier was essentially flat (about 0.5–0.6 $e/$Å^3) except for a peak of 1.68 $e/$Å^3 located 0.2 Å from H2.

All calculations were performed on a VAX-11 computer using SDP-PLUS.[10]

IV. DESCRIPTION OF THE STRUCTURE

Two nonequivalent Co atoms are coordinated by five bridging O atoms from HPO_3^{2-} ions and one terminal H_2O molecule forming distorted octahedra. The metals are

bridged by two distinct phosphite ions (P1 with one, P2 with no free O atoms) forming puckered layers parallel to the a-c plane (Fig. 1). Connections between layers are limited exclusively to H bonds between coordinated H_2O and the only free oxygen from phosphite (O2). There are also some hydrogen bonds of the same type as well as among water molecules within the layers.

The layers can be viewed as formed by zigzag chains of edge-sharing octahedra interconnected by a three-atom bridge (O4-P2-O5) and a single oxygen bridge (O6), from the same phosphite anion. This formal view is also supported by the three short Co1-Co2 separations, the two shortest (3.02, 3.15 Å) corresponding to intrachain, the longest (3.61 Å) to interchain separations.

V. MAGNETIC CHARACTERIZATION AND ANALYSIS

A full magnetic characterization of a $CoHPO_3 \cdot H_2O$ powdered sample, has been performed using ac magnetic susceptibility at zero dc field, $\nu = 110$ Hz, ac excitation fields, $H_0 = 1$ Oe, and temperatures between 4.2 and 150 K in both cooling and heating runs.

In Fig. 2, we have represented the in-phase, $\chi'(T)$, component of the ac susceptibility. In order to cover the three orders of magnitude of $\chi'(T)$, a semilogarithmic plot has been used. The most relevant experimental facts of the $\chi'(T)$ curve are the presence of a sharp peak at $T_c = (10.8 \pm 0.1)$ K, and the temperature change of $\chi'(T)$ which slowly increases upon lowering the temperature and close to T_c it crosses over and becomes almost divergent.

In the inset of Fig. 2, both components of the ac susceptibility, $\chi'(T)$ and $\chi''(T)$, have been represented in the neighborhood of T_c using an enlarged linear scale. In the plot, the data derived in the heating and cooling process have been included thus, within experimental reproducibility, the transition at T_c has continuous character (second order).

FIG. 2. Semilogarithmic plot of $\chi'(T)$ (in-phase) component of the ac susceptibility vs T. In the inset, both components of the ac susceptibility, $\chi'(T)$ and $\chi''(T)$, have been represented in the neighborhood of T_c using an enlarged linear scale.

The absorption, $\chi''(T)$, is zero down to T_c and at this temperature increases sharply and takes its higher value, about one-eighth of $\chi'(T)$, decreasing further with the temperature. $\chi''(T)$ is proportional to the B-H hysteresis loop area and thus it proves unambiguously that at T_c the system orders with a net magnetic moment.

A χT-vs-T representation shows a slow decrease in χT upon cooling down, reaching a minimum, and then increase abruptly. The presence of this minimum is indicative of a low-dimensional ferrimagnetic behavior, although the possibility of a weak ferromagnetism cannot be excluded.

An analysis of the $\chi T / C$ vs $\epsilon = (1 - T_c/T)$ data in the critical region, for $T > T_c$, using a double-logarithmic plot, yields a critical exponent $\gamma = 1.75$ for $0.01 < \epsilon < 0.1$, which corresponds to a two-dimensional (2D) Ising model.

This 2D behavior would be consistent with the layered character of the structure. The bonding between Co ions is different along the a and c directions. Each layer can be considered as formed by interconnected zigzag chains. Within each chain the stronger superexchange pathway is likely to be provided by the double oxygen bridge, as opposed to the O-P-O group. The interchain connections consist of alternating O-P-O and single oxygen bridges. Depending on the relative values of the intra- (J_x), and interchain (J_y) interactions the compound would display one- (1D) or two-dimensional (2D) characteristics. The fact that the interchain interactions are predominantly produced by the single oxygen bridges (plus O-P-O bridges), leading to longer Co···Co separations makes those likely to be weaker than the intrachain interactions. This suggests that, at high temperature, the compound would behave as a 1D system. On the other hand, the weakest of the three possible interactions must be J_z since this is only sustained by hydrogen bonds. The critical behavior points out, as expected from these considerations, that $|J_x|, |J_y| \gg |J_z|$.

On the other hand, the anisotropic behavior is consistent with the electronic structure of the Co(II) ion, since the high anisotropy of the lowest lying Kramer doublet of the
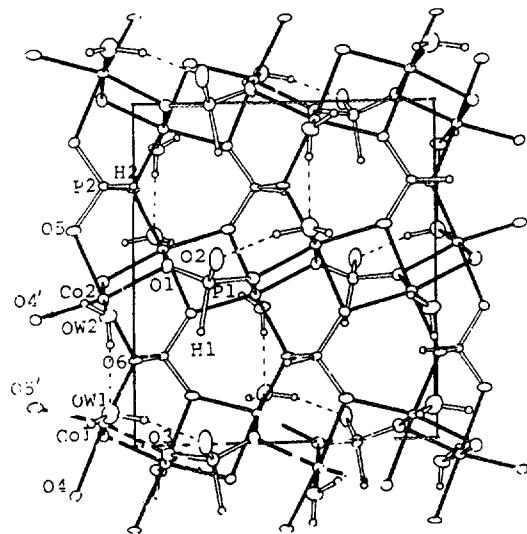

FIG. 1. Structure of one layer in $Co(HPO_3) \cdot H_2O$ viewed down the b axis. Relevant bond distances (in Å) are: Co1-OW1, 2.110(5); Co1-O1, 2.136(4); Co1-O3, 2.081(4); Co1-O4, 2.182(4); Co1-O5, 2.067(5); Co1-O6, 2.099(4); Co2-OW2, 2.056(5); Co2-O1, 2.085(4); Co2-O3, 2.057(4); Co2-O4, 2.046(4); Co2-O5, 2.185(4); Co2-O6, 2.189(4).
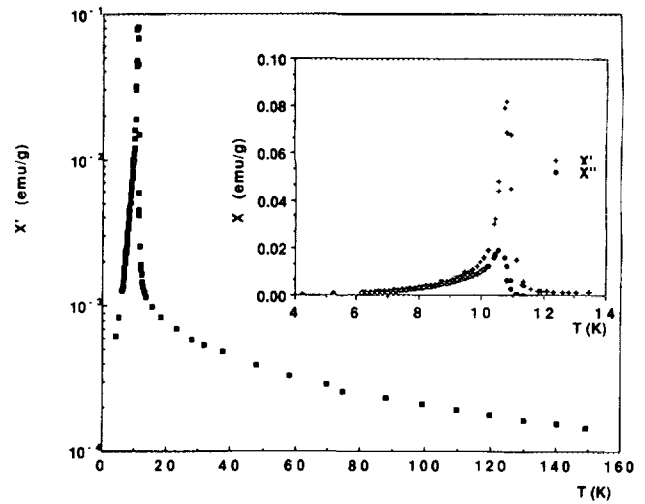
Co(II) ion (the only level populated at temperatures lower than ∼ 50 K), usually leads to anisotropic exchange interactions.[11,12]

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