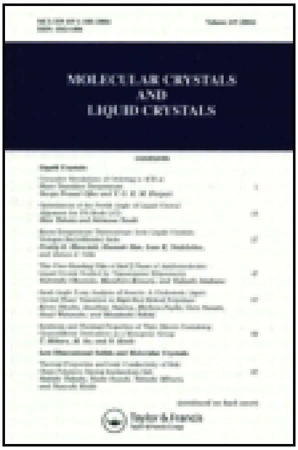

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Magnetic Ordering in Layered Cobalt-Hydroxide Triangular Lattices

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Magnetic Ordering in Layered Cobalt-Hydroxide Triangular Lattices

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(In final form July 9, 1999)

The synthesis and magnetic properties of a series of layered compounds, where the interlayer separation has been tuned from 9 to 28 Å, are reported. It is shown that the Brucite-type layered compounds of cobalt having octahedral sites only, $Co_2(OH)_3X$, are metamagnets, while those adopting the triple-deck structure, $Co_5(OH)_8(X)_2 \cdot x$solvent, containing both octahedral and tetrahedral sites are two-sublattice ferrimagnets. The long range ordering (LRO), T_C up to 60 K or T_N of 38 K, in both structural types is brought about by dipolar interaction between layers and super-exchange interactions between nearest neighbors within a layer. The exceptional hardness of these two structural types, coercive field of 20,000 Oe for the ferrimagnets and greater than 50,000 Oe for the metamagnet, is due to the synergy of single-ion and crystalline shape anisotropies and, most importantly, the alignment of the moments perpendicular to the layer.

Keywords: magnets; layered; high coercive field; cobalt; clay

INTRODUCTION

The area of solid state chemistry dealing with the search for long range magnetic ordering in metal-organic hybrid compounds has acquired much attention in the last few years [1,2]. This has been fuelled by the synthesis of a wide range of materials and to the success in the design of multitopic ligands to achieve the desired structures. In infinite lattices the first requirement for the observation of LRO is the relative alignment of the magnetic orbital of near

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neighbors [3,4]. The second is the magnitude of the exchange interaction which depends on the nature of the bridging unit, usually the organic moiety between the inorganic magnetic centers. A simple correlation exists for the Curie temperatures (T_C) of 3D lattices where all nearest neighbors are connected through equivalent bridging connectors. For pure metals (no bridging unit) T_C is ~1400 K [5], for those with one atom connector (*e.g.*: oxides) T_C is ~800 K [5] and for those with two atoms connectors (*e.g.*: cyanides of the Prussian blue family) T_C is 315 K [6]. We [7] and others [8,9] have recently prepared and characterized the first series of transition metals complexes, based on the dicyanamide ligand (N≡C–N–C≡N), having a three atoms bridge, ···N–C≡N···, between the centers; the highest T_C observed is 21 K. It is clear that increasing the size of the bridging units will not result in high Curie temperatures.

While searching for novel magnetic materials, we have found that the reaction of an aqueous solution of a divalent metal nitrate with ammonium hydroxide in the presence of dodecylsulfonate, produces layered $M_2(OH)_3(C_{12}H_{25}SO_3)\cdot H_2O$, M = Cu or Ni and $M_5(OH)_8(C_{12}H_{25}SO_3)_2\cdot 5H_2O$, M = Co or Zn [10]. The interlayer spacing is ~25 Å. The copper compound exhibits short range antiferromagnetic coupling, while the nickel compound is a ferromagnet (T_C = 18 K and H_{co} = 400 Oe) and the cobalt compound behaves as a ferrimagnet (T_C = 58 K and H_{co} = 19,000 Oe). These unusual observations of LRO for layers at such large distances was explained by a combination of super-exchange interactions between nearest neighbors within the layer and dipolar interaction between layers. We have consequently synthesized compounds with a range of anions, alkyl-carboxylates, -dicarboxylates, -sulfates, -sulfonates and polycyanides, to study the effect of the anions and the interlayer spacing on the critical temperature and on the magnetic hardness. We also found in addition to $Co_5(OH)_8(\text{terephthalate})\cdot 2H_2O$ a second structural type having the formula $Co_4(OH)_2(\text{terephthalate})_3\cdot(NH_3)_{1.5}(H_2O)_{2.5}$ [11], which is a metamagnet displaying a wide hysteresis loop and a coercive field in excess of 50,000 Oe. Here, we highlight their syntheses, characterizations and magnetic properties.

EXPERIMENTAL

$Co_5(OH)_8(X)_2 \cdot x$solvent were prepared by adding 3 ml of ammonium hydroxide (30%) drop-wise to a solution of $Co(H_2O)_2(NO_3)_2$ (3 g) and either the acid or the sodium salt of the acid (1 g) in 200 ml of a 1:1 mixture of distilled water and absolute ethanol at 40°C. Dark blue to green precipitates are formed which were collected by filtration, washed with water, ethanol and acetone and dried in air. Similar compounds were also prepared by the reaction of a suspension of $Co_2(OH)_3(NO_3)$ in water with the sodium salt of the acid at 25°C for 24 hours.

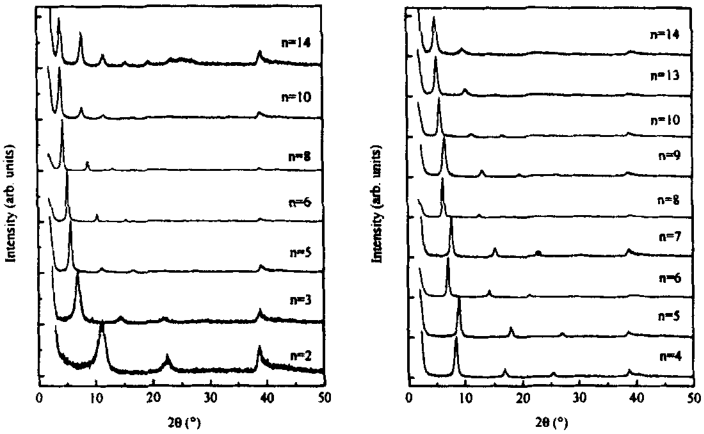
$Co_2(OH)_3(NO_3)$ was prepared as a pink solid by the literature procedure [12]. $Co_4(OH)_2(\text{terephthalate})_3 \cdot (NH_3)_{1.5}(H_2O)_{2.5}$ was prepared by mixing $Co(H_2O)_6(NO_3)_2$ (3g), sodium terephthalate (1g) and 3 ml of aqueous ammonia (30%) in a warm (40°C) solution of 250 ml of water and absolute ethanol (1:1 mixture). A blue green precipitate was produced which was transformed into the pink compound by reducing the solution volume to 60 ml at 80°C. The compounds were authenticated by chemical and thermogravimetric analyses.

RESULTS AND DISCUSSION

Syntheses

The reaction of cobalt nitrate with a base in the presence of a range of anions (X) results in layered compounds of general formula: $Co_5(OH)_8(X)_2 \cdot xH_2O$. The reaction of solid $Co_2(OH)_3(NO_3)$ with $NaN(CN)_2$ in water produces the same compound, $Co_5(OH)_8(N(CN)_2)_2 \cdot 6H_2O$, as that obtained by the reaction of ammonia with cobalt nitrate in the presence of $NaN(CN)_2$. It is also obtained by the reaction of a suspension of $Co^{II}(N(CN)_2)_2$ in water with ammonia. It is therefore unlikely that the reaction of an alkyl-carboxylate or -sulfate with $Co_2(OH)_3(NO_3)$ is the process of 'intercalation' or 'anion exchange' [13].

X-ray Powder Diffraction, Electron Diffraction and Structure



(a) (b)

FIGURE 1 Powder X-ray diffraction of (a) $Co_5(OH)_8(C_nH_{2n-1}O_2)\cdot xH_2O$ and (b) $Co_5(OH)_8(C_nH_{2n-4}O_4)\cdot xH_2O$ (Co-Kα1, λ = 1.789Å).

The XRD patterns for the carboxylate and dicarboxylate compounds are shown in Fig. 1. The patterns are dominated by a progression of the *00ℓ* Bragg reflections corresponding to the basal spacing characteristic of layered structures and two asymmetric broad in plane reflections at d = 2.69 and 1.55 Å. In some cases there is an extra reflection at d = 6.25 Å which may correspond to one in-plane crystallographic axis and is twice the M-M distance of the triangular Brucite-like layer. The basal spacing (d_{00l}) increases with the length of the anion (Fig. 2); for the dicarboxylates a pronounced alternation is observed for odd and even chain lengths due to the switching of the orientation of the carboxylate group. The difference in spacing between a carboxylate and a dicarboxylate having the same number of carbon atoms in the chain is ~6 Å, implying that the dicarboxylate bridges adjacent layers. Further structural information were obtained by electron diffraction. The pattern observed for a microcrystal of $Co_5(OH)_8(N(CN)_2)_2\cdot 6H_2O$ exhibits two rings on which the most intense Bragg reflections are superposed. Within each ring there are six main spots. The estimated spacing of the inner and outer rings are 2.7 and 1.6 Å, respectively; in good agreement with those observed in the XRD data. The pattern can be simulated by using the atomic coordinates and cell parameters of the known monoclinic form of $Zn_5(OH)_8(H_2O)_2(NO_3)_2$ [14] suggesting that the two compounds are isostructural (Fig. 3).

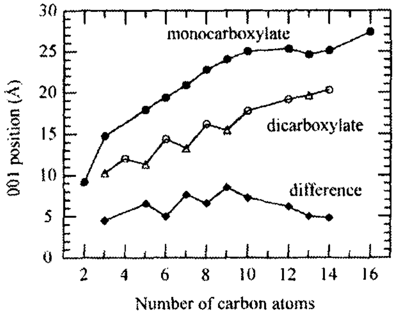


FIGURE 2 The dependence of d_{001} as a function of the number of carbon atoms (n) in the chain.

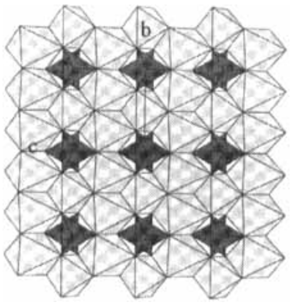


FIGURE 3 Triple-deck layer structure $Zn_5(OH)_8(H_2O)_2(NO_3)_2$ [14] showing the layer of octahedral cobalt (grey) sandwiched by tetrahedral cobalt (dark).

$Co_4(OH)_2(\text{terephthalate})_3{\cdot}(NH_3)_{1.5}(H_2O)_{2.5}$ crystallises in the following unit cell: a = 9.97(1), b = 11.24(1), c = 6.29(1) Å, β = 95.95° where the a-parameter corresponds to the interlayer separation, b-parameter to $4 \times r \sin \pi/3$

and the c-parameter to 2 × *r*, where r is the Co-Co distance (3.15 Å). The magnitude of the a-parameter is in good agreement with the sum of two Co-O bonds (~2 Å) and the distance (7.4 Å) between terminal oxygen atoms of the terephthalate, suggesting it adopts a layer structure similar to that of $Co_2(OH)_3(NO_3)$.

X-ray Absorption Spectroscopy

The cobalt K-edge XAS spectra of $Co_5(OH)_8(C_7H_{15}CO_2)_2 \cdot 4H_2O$, $Co_5(OH)_8(N(CN)_2)_2 \cdot 6H_2O$ and of the reference Co^{II} compound, $Co_2(OH)_3(NO_3)$, have been recorded at 80 K on the LURE synchrotron ring. The pre-edge feature, originating from the 3d ← 1s transition, is observed at 7702 eV and the K-edge at 7719 eV for $Co_2(OH)_3(NO_3)$ and at 7715 and 7719 eV for $Co_5(OH)_8(C_7H_{15}CO_2)_2 \cdot 4H_2O$ and $Co_5(OH)_8(N(CN)_2)_2 \cdot 6H_2O$. The presence of tetrahedral coordinated Co^{II} is confirmed by the more intense pre-edge feature for $Co_5(OH)_8(C_7H_{15}CO_2)_2 \cdot 4H_2O$ and $Co_5(OH)_8(N(CN)_2)_2 \cdot 6H_2O$ [15]. The lack of any peak at 7722 eV excludes the presence of trivalent cobalt.

Infrared and UV-Vis Spectroscopies

The infrared spectra were used to identify the presence of the anions and its mode of coordination to the Co-OH layers. The energies of the asymmetric and symmetric vibrations of the carboxylate groups are consistent with a monodentate coordination for both structural types [16]. The observation of only one of each for the dicarboxylate compounds suggests that the two terminal carboxylate groups are equivalent and they bridge the cobalt atoms of adjacent layers. Three C-N stretching modes of the dicyanamide ion are observed at 2271, 2249 and 2211 cm^{-1} in good agreement with a dicyanamide coordination through only one of its nitrogen atoms.

The UV-vis spectra of the two types of compounds are quite distinct; the pink compounds show weak d-d absorption corresponding to $^4A_{2g}(P) \leftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ of Co^{II} in octahedral coordination of a weak ligand and the green and blue compounds show two additional sharp peaks at lower energies corresponding to $^4T_1(P) \leftarrow {}^4A_2$ transition of Co^{II} in tetrahedral coordination geometry which is split by spin-orbit coupling [17]. The spectra do not show any bands originating from Co^{III} which should show two bands at ~29,000 ($^1T_{1g} \leftarrow {}^1A_{1g}$) and ~20,000 cm^{-1} ($^1T_{2g} \leftarrow {}^1A_{1g}$).

Magnetic Properties

The temperature dependence of the product of susceptibility and temperature and of the inverse susceptibility of four representative $Co_5(OH)_8(X)_2.x$solvent are shown in Fig. 4. All behaves in a similar manner; their moment decreases to a minimum at ~120 K as the temperature is lowered from room temperature, followed by a continuous rise to a maximum at ~50 K. This behavior is typical of ferrimagnets. The data in the range 150-300 K fit the Curie-Weiss law with C = 13.0±0.5 cm^{3}K/mol and Θ varies between -30 and -75 K. The Curie constants are in good agreement with that expected for the sum of three octahedral and two tetrahedral Co^{II} ions. The negative Weiss temperatures suggest dominant short range antiferromagnetic exchange.

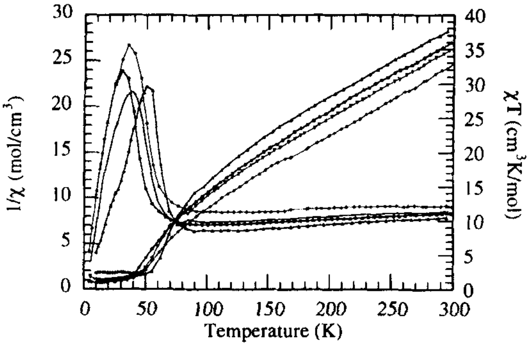


FIGURE 4 Temperature dependence of the inverse susceptibilities and of the products of susceptibility and temperature measured in applied field of 12,000 Oe for $Co_5(OH)_8(X)_2{\cdot}4H_2O$ where $(X)_2$ = fumarate, succinate or isophthalate, and X = adamantane carboxylate.

The AC and DC magnetization in near zero applied field (1 Oe) in the ordered state and around the critical temperature region are shown in Fig. 5. Spontaneous magnetization is observed by a sharp increase of the DC magnetization and by a peak in both the real and imaginary components of the AC magnetization. For most compounds there is an additional increase of the DC magnetization at ~30 K, which is accompanied by a weaker peak in the AC magnetization. This may be due to the presence of a slight amount of another phase, *e.g.*: the hexagonal form [14].

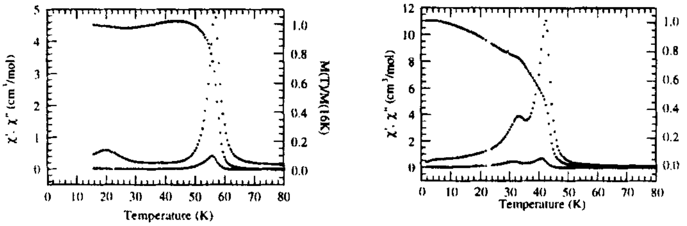


FIGURE 5 Temperature dependence of the DC and AC magnetization of $Co_5(OH)_8(succinate)\cdot 4H_2O$ (left) and $Co_5(OH)_8(isophthalate)\cdot 5H_2O$ (right).

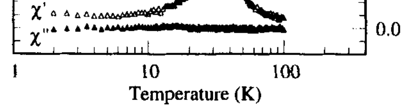
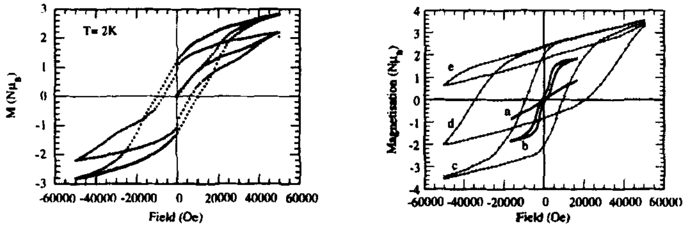


FIGURE 6 Temperature dependence of the DC and AC susceptibilities of $Co_4(OH)_2(terephthalate)_3\cdot(NH_3)_{1.5}(H_2O)_{2.5}$.

The magnetic susceptibility of $Co_4(OH)_2(terephthalate)_3\cdot(NH_3)_{1.5}(H_2O)_{2.5}$ is field dependent. In a small applied field both AC and DC susceptibilities increase to a maximum at T_N (38 K) and in a DC-field of 5000 Oe, larger than the critical field, it increases to a saturation plateau (Fig. 6) [18]. The Curie constant derived from a Curie-Weiss fit of the inverse susceptibility versus temperature for T>150 K gives C = 11.86(3) cm^3K/mol and Θ = -67(1) K. The decrease from high temperature to 90 K is due to the effect of spin-orbit coupling, followed by an increase due to short range ferromagnetic interactions between the cobalt atoms within the layer becoming more important than spin-orbit coupling. At 38 K LRO sets in due to antiferromagnetic interactions between moments in adjacent layers. In a field higher than the anisotropy field, the moments are forced to be parallel. The real part of the AC susceptibility shows a peak of magnitude similar to that observed in low DC field and no anomaly is observed for the imaginary component, as expected for antiferromagnets.



(a) (b)

FIGURE 7 Isothermal magnetization of $Co_5(OH)_8(succinate)\cdot 4H_2O$ and $Co_5(OH)_8(isophthalate)\cdot 5H_2O$ at 2 K (left) and of $Co_4(OH)_2(terephthalate)_3\cdot(NH_3)_{1.5}(H_2O)_{2.5}$ at (a) 50 K, (b) 17.5 K, (c) 10 K, (d) 5 K and (e) 2 K (right).

Below the transition temperature the isothermal magnetization of all the $Co_5(OH)_8(X)_2\cdot xH_2O$ compounds are characterized by hysteresis loops (Fig. 7a) with coercive field approaching 20,000 Oe at 2 K. In most cases the magnetization is still increasing in field of 50,000 Oe, due to incomplete reversal of the moments which suggests that the anisotropy field is large. The wide hysteresis is due to the large magneto-crystalline anisotropy which is derived from the synergy of several factors: (a) large single-ion anisotropy for cobalt, (b) shape anisotropy and (c) the alignment of the moment perpendicular to the layers. The value of the magnetization in field of 5 tesla approaches $3\mu_B$ which is consistent with the proposed structure comprising of two antiferromagnetically coupled sublattices within a layer; one comprising of cobalt in octahedral sites (3 per formula unit) and the other in tetrahedral sites (2 per formula unit).

Isothermal magnetization of $Co_4(OH)_2(terephthalate)_3{\cdot}(NH_3)_{1.5}(H_2O)_{2.5}$ at several temperatures is shown in Fig. 7b. At high temperatures ($T > T_N$) the magnetization is linear and reversible as for paramagnets while just above T_N there is a slight curvature that is a typical signature of short range ferromagnetic interactions. Just below T_N the magnetization takes an S-shape (Fig. 7b) and remains reversible. The critical field to align the moments parallel increases as the temperature is lowered. At 22.5 K and below the isothermal magnetization exhibits hysteresis. The unusual feature of $Co_4(OH)_2(terephthalate)_3{\cdot}(NH_3)_{1.5}(H_2O)_{2.5}$ is that there is a large remanent magnetization and a large coercive field (attaining in excess of 5 Tesla at 2 K) below the tricritical temperature of 22.5 K unlike known metamagnets [19]. Figure 7 also show the first magnetization after zero-field cooling (ZFC) and the hysteresis loops after field cooling (FC) the sample in 5 Tesla from 100 K to the measuring temperature.

The LRO in the two structural types occurs at surprisingly high temperatures (T_C of 58 K and T_N of 38 K) for layers separated by as much as 28 Å. The magnetic exchange interaction between cobalt on adjacent layers is expected to be negligible and even if the layers are covalently bridged the exchange interaction through bonds is expected to follow a R^{-10} dependence [20], where R is the distance between the spin centers. On the other hand purely electrostatic dipolar interaction between the layers is proportional to R^{-3}, which becomes more important at large distance. A dipolar mechanism becomes more effective at large distance if the moments are large [21]. For the layered compounds, this is achieved by super-exchange interactions between nearest neighbors. As the temperature is lowered the correlation length within the layer, which depends on the magnitude of the near-neighbor exchange, increases. The main difference between the two structural types is that the dipolar interaction is ferromagnetic between layers for the $Co_5(OH)_8(X)_2{\cdot}xH_2O$ compounds but is antiferromagnetic for $Co_4(OH)_2(\text{terephthalate})_3{\cdot}(NH_3)_{1.5}(H_2O)_{2.5}$.

CONCLUSION

Two structural types of cobalt hydroxide layered compounds have been synthesized and characterized. One consists of only octahedral Co^{II} and single Brucite layers while the other contains in addition tetrahedral Co^{II}. The former behaves as metamagnets exhibiting unusually large coercive fields and those of the latter are ferrimagnets. LRO is observed at temperatures which are weakly dependent on the interlayer spacing and the chemical or physical nature of the anions. Dipolar interaction between layers is proposed to be responsible for the LRO. The large coercive field is associated with the synergetic alignment of the moments perpendicular to the layers and to the crystallite shape and single-ion anisotropies.

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