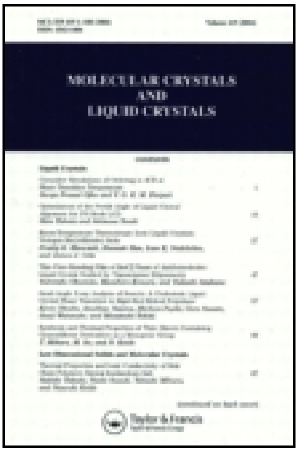

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A Novel Synthetic Route to Transition Metal Carbonates: Magnetic Properties Revisited

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A Novel Synthetic Route to Transition Metal Carbonates: Magnetic Properties Revisited

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ABSTRACT

We present a novel method for the preparation of transition metal carbonates that is able to provide solid solutions of controlled proportions. Unexpected magnetic properties, such as negative magnetization, for the mixed-metal solid solutions are observed that can be accounted to clustering. The negative magnetization is discussed in terms of dipolar interaction between neighboring clusters.

Keywords: carbonates, cobalt, magnetic properties, nickel, random fields.

INTRODUCTION

Transition metal-carbonates are mostly obtained naturally in the form *calcite*. The metal contents of these natural carbonates depend on the origin and the age of the rocks. In most cases, they contain different proportion of manganese, cobalt, nickel, iron, magnesium, zinc and calcium and traces of other heavy metals. On the one hand, one of the advantages of the presence of different ions is in the crystallization of large crystals and secondly, they provide various colored calcites. The disadvantage is that the crystals are of varying metal content; for example the core, the junctions and the surface of the crystals have different metal contents. Consequently, their magnetic properties are difficult to understand [1, 2]. Previous magnetic studies were made on these crystals and were found to be one of the first families for which canted antiferromagnetism (weak ferromagnetism) were observed [2]. Based on these early measurements Dzyaloshiinsky proposed his theoretical *antisymmetric-exchange* model to explain the occurrence of canting [3].

Several synthetic routes have been developed dating as far back as 1850 to produce pure single metal carbonate [4] and most of them use high-pressure carbon dioxide and sodium carbonate. For example, the best crystalline compounds were obtained by treating a solution of a metal dichloride with sodium carbonate in a sealed tube at 150°C under a positive pressure of carbon dioxide. However, this technique requires very special skills to seal tubes under high pressure of carbon dioxide. Our new synthetic procedure overcomes these difficulties by producing both the carbonate and the carbon dioxide *in situ* in sealed hydrothermal bombs [5].

Previous studies of the magnetic properties and magnetic structures of these synthetic compounds have revealed their true characteristic [2]. While iron carbonate is an antiferromagnet with the easy axis parallel to the trigonal axis, nickel and cobalt carbonate are canted-antiferromagnets with the easy axis lying in the basal plane [6]. We have studied the parent compound prepared by our modified technique and a series of mixed binary-metal carbonates where both metals are magnetic or one is magnetic and the other is not. Surprising results were observed with segregated transition temperatures and negative magnetization [7] in limited temperature regions. A model comprising dipolar interaction between islands of parent carbonates is developed to explain some of the observations.

EXPERIMENTAL

The syntheses were performed in 125 mls capacity teflon-lined hydrothermal bombs. Two different approaches were employed. The first consists of dissolving a total of 10g of metal nitrate or appropriate mixture of metal nitrates, 15g of sodium dicyanamide in 90mls of distilled water. The mixture is placed in the bombs, sealed and heated to 200°C for 2 days. The second approach uses the rutile form of metal bis(dicyanamide) [8] as the starting material. The compounds were characterized by elemental analyses, DT-TGA and infrared spectroscopy.

The magnetic measurements of the complexes were studied by a Quantum Design MPMS-XL SQUID magnetometer in the temperature range 2 - 300 K and fields up to 5 Tesla and Princeton Applied Research Vibrating Sample magnetometer. X-ray powder diffraction data were collected on a Siemens D-500 diffractometer with Co Ka (1=1.798Å) radiation at room temperature.

RESULTS AND DISCUSSION

The reaction of dicyanamide and water at temperatures above 150°C under pressure produces carbon dioxide, carbonate ion and ammonia as follows:

$$2\,C_2N_3^- + 9H_2O \longrightarrow CO_3^{2-} + 6NH_3 + 3CO_2$$

The reaction is slow and therefore generates the carbonate and carbon dioxide slowly to form well-formed hexagonal plates of maximum dimension of 10 microns. The pure cobalt is dark purple and the nickel is green. The mixed cobalt-nickel compounds display intermediate colors (*e.g.* light brown for the 1:1 mixture). Although chemical analyses, infrared and X-ray powder diffraction is consistent with the proportion of metals expected, EDX indicates the crystals have variable metal content. It is not certain if only the surface of the crystals has different metal content.

The crystal structure belongs to the hexagonal system, *R*-3c with a=4.6 and c=15.3Å. The diffraction patterns of the compounds were refined using FULLPROF with the coordinates of *siderite* as a starting point. The refined position and volumes and lattice parameters are consistent to those reported and show a continuous contraction of the lattice from pure $CoCO_3$ to pure $NiCO_3$ as expected due to the reduction of the ionic radius of nickel [9]. The structure consists of stacks of layers (figure 1) of MO_6 and CO_3. Each layer is connected to adjacent layers via the oxygen atoms resulting in a 3d-network of metal atoms connected by one oxygen atom bridges.

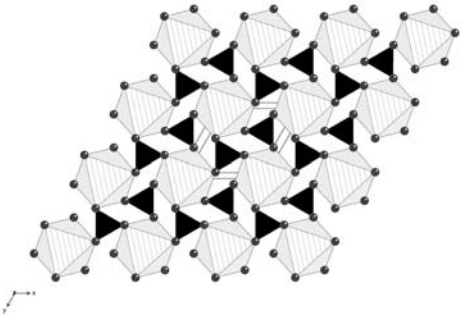

FIGURE 1: Arrangement of the MO_6 and CO_3 units in a layer of MCO_3.

The magnetic properties have been studied in the temperature range 2-300K in different applied magnetic field up to 100 Oe and their isothermal magnetization at 2K in field of ±5Tesla. The susceptibility of the pure cobalt and nickel compound, their solid solutions and those diluted in $MgCO_3$ exhibit similar behavior in the paramagnetic region with negative Weiss constants consistent with those reported. The effective moment for the Ni-Co solid solutions increases linearly from that of pure Ni to that of pure Co. The parent compounds show spontaneous magnetization at the long-range magnetic ordering temperatures of 18K (Co) and 23K (Ni). The diluted Mg solid solutions exhibit the same critical temperatures. However, the mixed Ni-Co solid solutions display the two segregated transitions at the same temperatures in contrast to the expected one intermediate transition. The low field data are shown in figure 2 for the parent compounds, the solid solution $Ni_{0.5}Co_{0.5}CO_3$ and of a sample made up of 50%$NiCO_3$ and 50%$CoCO_3$. The temperature dependence of the magnetization is independent of field for the parent compounds and is very field dependent for the Mg diluted compounds and the Ni-Co solid solutions. An example is shown for

$Ni_{0.5}Co_{0.5}CO_3$ in figure 3. The observed peaks disappear on increasing the applied field.

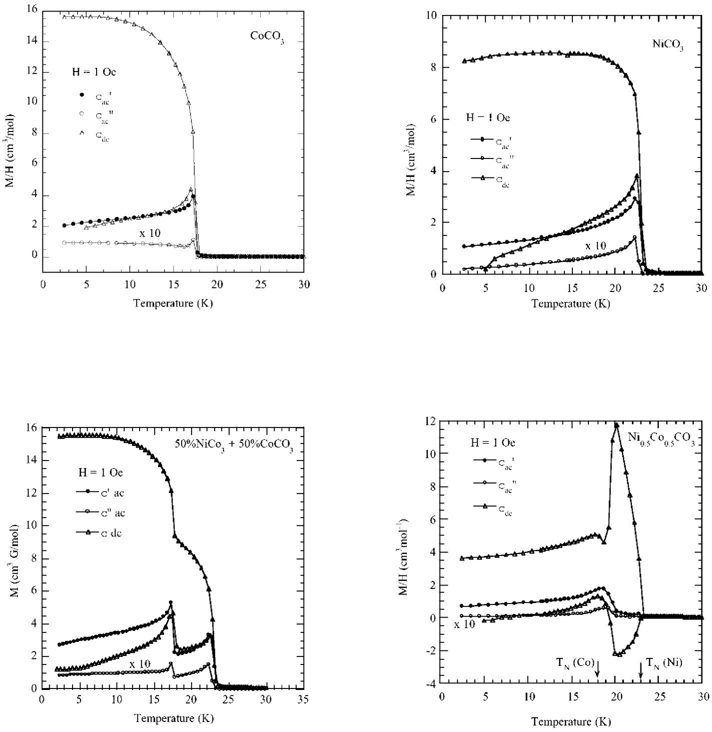

FIGURE 2: ZFC-FC dc-magnetization and FC ac-magnetization (20Hz) in 1 Oe.

The spontaneous magnetization of the nickel and cobalt carbonates is well understood as canted antiferromagnetism with the moments in the basal plane perpendicular to the trigonal axis. The presence of segregated transition temperatures in the Ni-Co solid solutions suggest that the samples are not homogeneous and therefore does not have percolation threshold but consist of clusters of the two components [10]. However, their magnetic behaviors are not simply a superposition of the behavior of the two components as shown by a mixture of the parent compounds (figure 2). Their unusual magnetic behavior can be understood by the presence of dipolar interactions between the clusters. For example, when the $Ni_{0.5}Co_{0.5}CO_3$ sample is warmed in a small field after zero field cooling the magnetization increases as the cobalt rich clusters become soft, it then goes negative due to anti-parallel alignment of the nickel rich clusters. The situation is reversed on cooling in the same field. It first increases due to LRO in the Ni-rich clusters and as the Co-rich clusters order it align anti-parallel to the Ni and thus the magnetization displays a large drop. This explanation is also true to the Mg-diluted samples, where the magnetization decreases below the transition temperatures due to anti-parallel alignment of smaller clusters relative to large ones. As the applied magnetic field exceeds the average dipolar field the clusters are aligned with their moments parallel.

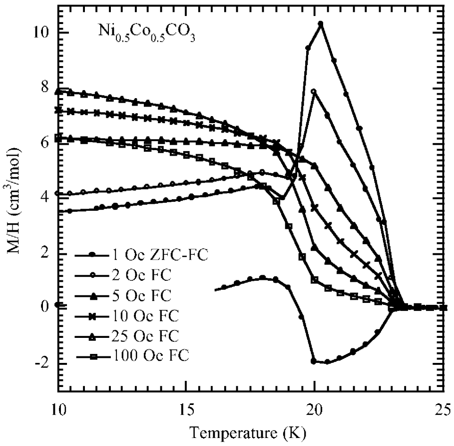

FIGURE 3: dc-magnetization on cooling in different applied fields.

The isothermal magnetization at 2K exhibits a linear variation with field above 1 tesla and a hysteresis loop with a coercive field of up to 200 Oe. We note that the solid solutions and Mg-diluted samples display larger coercivity than the parent compounds.

CONCLUSION

A clean and easy synthetic procedure is described for the preparation of transition metal carbonates. Their magnetic properties are described as canted antiferromagnetism. The samples are composed of clusters that interact by a dipolar field of the order of 5 Oe.

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