Weak ferrimagnetism, compensation point and magnetization reversal in $Ni(HCOO)_2 \times 2H_2O$

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Abstract

Nickel (II) format dihydrate $Ni(HCOO)_2 \times 2H_2O$ shows peculiar magnetic response at $T < T_N = 15.5$ K. The magnitude of weak magnetic moment increases initially below T_N, equals zero at $T^* = 8.5$ K and increases again at lowering temperature. The sign of low field magnetization at any given temperature is determined by the sample's magnetic prehistory and the signs are opposite to each other at $T < T^*$ and $T^* < T < T_N$. This behavior suggests that $Ni(HCOO)_2 \times 2H_2O$ is a weak ferrimagnet and T^* is a compensation point.

The nickel (II) formate dihydrate $Ni(HCOO)_2 \times 2H_2O$ crystallizes in monoclinic $P2_1/c$ spacegroup and include four formula units in the unit cell with $a = 8.60$ Å, $b = 7.06$ Å, $c = 9.21$ Å, $\beta = 96.5^\circ$ [1]. The structure contains two nonequivalent subsystems of Ni^{2+} ions and the oxygen octahedrons coordinating the Ni_1 and Ni_2 ions are tilted with respect to each other within both subsystems.

The temperature dependencies of magnetization of $Ni(HCOO)_2 \times 2H_2O$ powder sample taken in zero-field-cooling (ZFC) and field-cooling (FC) regimes at $H = 0.01$ T are shown in Fig. 1. The inset to this figure shows temperature dependence of inverse magnetic susceptibility in a wide temperature range. Evidently, the main exchange interaction in $Ni(HCOO)_2 \times 2H_2O$ is antiferromagnetic. At heating in ZFC regime the sample shows firstly large "paramagnetic" response at low temperatures, then the magnetic moment gradually decreases with increasing temperature, changes to "diamagnetic" at $T^* = 8.5$ K, and once again became paramagnetic above $T_N = 15.5$ K. At subsequent cooling in FC regime the magnetic behavior of the sample at low temperatures appears to be mirror-like with respect to magnetization sign as compared with ZFC measurements.

The magnetization curves taken in ZFC regime in the range 2 – 15 K are ferromagnetic-like, i.e. they show spontaneous magnetic moment, are weakly nonlinear at low fields and tend to linear dependences at high magnetic field. The absolute values of magnetization are by two orders of magnitude smaller than that corresponding to parallel alignment of Ni^{2+} magnetic moments. Therefore, the experimental data presented suggest that below T_N a weakly ferrimagnetic state is realized in $Ni(HCOO)_2 \times 2H_2O$, and T^* is a compensation temperature.

The analysis of the magnetic superexchange pathways in nickel formate dihydrate shows that the nickel ions in Ni_1-subsystem are connected to each other and to nickel ions in Ni_2-subsystem. There are no superexchange pathways within the Ni_2 subsystem, meaning that in the absence of $Ni_1 - Ni_2$ exchange interactions the Ni_2 subsystem can be considered paramagnetic.

The model suggested for the appearance of weak ferrimagnetism and compensation point in $Ni(HCOO)_2 \times 2H_2O$ is as follows. Weak ferrimagnetism arises from the competition of weak ferromagnetic moments of two nonequivalent antiferromagnetic Ni_1 and Ni_2 subsystems. The compensation point is due to the difference in temperature dependencies of weak ferro-

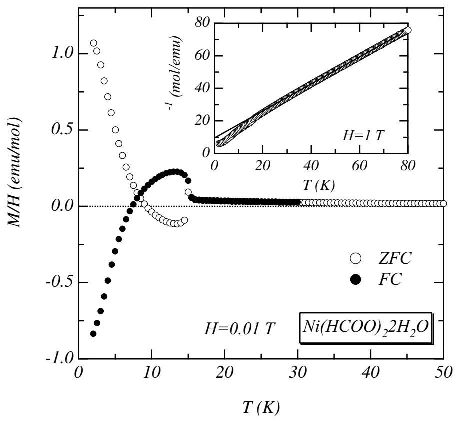

Fig. 1. The temperature dependencies of magnetization of $Ni(COOH)_2 \times 2H_2O$ at $H = 0.01$ T taken in zero-field-cooling (o) and field-cooling ($\bullet$) regimes.

magnetic moments of Ni_1 and Ni_2 subsystems. The deviations from antiparallel alignment of magnetic moments within these subsystems are caused by single ion anisotropy. At cooling below the Neel temperature the weak magnetization of Ni_1 subsystem exceeds that of Ni_2 subsystem. This occurs because M_1(T) dependence is much steeper than M_2(T) dependence in vicinity of T_N. At further cooling the values of Ni_1 and Ni_2 sublattice magnetizations approach each other. If magnetic anisotropy in Ni_2 subsystem is "larger" than that of Ni_1 subsystem, at low temperatures the weak magnetization of Ni_2 subsystem will prevail.

In conclusion, the phenomena of weak ferrimagnetism is found in nickel (II) formate dihydrate $Ni(HCOO)_2 \times 2H_2O$ containing only one type of magnetic ions. These ions constitute two canted antiferromagnetic subsystems whose competition results in compensation point and magnetization reversal.

References

[1] von K. Krogmann and R. Mattes, Z. Krist. **118** (1963) 291.