Weak ferrimagnetism, compensation point and magnetization reversal in Ni(HCOO)₂ × 2H₂O

H. Kageyama¹, D.I. Khomskii², R.Z. Levitin³, A.N. Vasiliev³,*

¹ Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
² Solid State Physics Laboratory, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
³ Physics Faculty, Moscow State University, Moscow 119899, Russia

Abstract

Nickel (II) formate dihydrate Ni(HCOO)₂ × 2H₂O 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 Ni magnitude of weak magnetic moment increases initially below Ni₂ structure contains two nonequivalent subsystems of r₂₀₀₃ Elsevier Science B.V. All rights reserved.

weak ferrimagnetism and compensation point in 2H₂O is a weak ferrimagnet and T* is a compensation point.

© 2003 Elsevier Science B.V. All rights reserved.

The nickel (II) formate dihydrate Ni(HCOO)₂ × 2H₂O crystallizes in monoclinic P2₁/c spacegroup and include four formula units in the unit cell with a = 8.60 Å, b = 7.06 Å, c = 9.21 Å, β = 96.5° [1]. The structure contains two nonequivalent subsystems of Ni²⁺ ions and the oxygen octahedrons coordinating the Ni₁ and Ni₂ ions are tilted with respect to each other within both subsystems.

The temperature dependencies of magnetization of Ni(HCOO)₂ × 2H₂O 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 × 2H₂O 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 non-linear 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 Ni²⁺ magnetic moments. Therefore, the experimental data presented suggest that below T_N a weakly ferrimagnetic state is realized in Ni(HCOO)₂ × 2H₂O, and T* is a compensation temperature.

The analysis of the magnetic superexchange pathways in nickel formate dihydrate shows that the nickel ions in Ni₁-subsystem are connected to each other and to nickel ions in Ni₂-subsystem. There are no superexchange pathways within the Ni₂ subsystem, meaning that in the absence of Ni₁–Ni₂ exchange interactions the Ni₂ subsystem can be considered paramagnetic.

The model suggested for the appearance of weak ferrimagnetism and compensation point in Ni(HCOO)₂ × 2H₂O is as follows. Weak ferrimagnetism arises from the competition of weak ferromagnetic moments of two nonequivalent antiferromagnetic Ni₁ and Ni₂ subsystems. The compensation point is due to the difference in temperature dependencies of weak ferromagnetic moments of Ni₁ and Ni₂ 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)$_2$·2H$_2$O containing only one type of magnetic ions. These ions constitute two canted antiferromagnetic subsystems whose competition results in compensation point and magnetization reversal.

References