Study on Magnetic Properties of Vermiculite Intercalation compounds

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I.   INTRODUCTION

In recent years the study of two-dimensional (2D) phenomena is one of the major themes of condensed matter physics. This effort has naturally centered around intercalation compounds with host materials having low dimensional open crystalline structures. The open crystalline structures take the 2D ordered form for graphite and layered silicates such as vermiculite. Like GIC's, vermiculite intercalation compounds (VIC's) will provide as interesting a system as the well-studied intercalation systems. The VIC's are well-characterized expanding layered silicates which offer the unique characteristic of forming water layers within an interlamellar space between the silicate layers. The silicate layers of VIC's are composed of two tetrahedral sheets coupled symmetrically to an octahedral sheet, and have a net negative charge due to isomorphic substitution of Al^{3+} ions in the Si^{4+} sites of the tetrahedral sheets. This charge deficiency is compensated by cations located midway in the interlamellar space. Various cations and molecules can be intercalated without drastically changing the host layers.[1] In the pristine vermiculite which occurs in nature, the Mg^{2+} ions occupy the interlamellar space (Mg-VIC).

Naturally occurring vermiculite has Mg^{2+} ions as cations and is denoted by Mg^{2+} VIC. The Llano vermiculite used for our experiments has the unit-cell stoichiometry

$$(Si_{5.72} Al_{2.28}) (Mg_{5.88} Al_{0.10} Fe_{0.03} Ti_{0.02}) O_{20} (OH)_4 Mg_{0.93} (H_2O)_v . \quad (1)$$
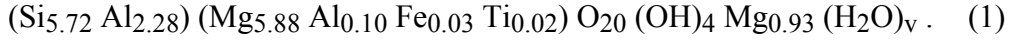
The Mg^{2+} ions can be easily replaced by various kinds of intercalant species such as transition metal ions (Ni^{2+}, Co^{2+}, Mn^{2+}, and Cu^{2+}) and rare earth metal ions (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+}). The magnetic VIC's have three kinds of hydration states defined by the number of water layers in the interlamellar space; 0-, 1-, and 2-water layer hydration states (WLHS). In the 1-WLHS the water molecules normally lie in the same plane as the cations. In the 2-WLHS, the magnetic cations are usually sandwiched between upper and lower water layers. The hydration state depends on the water vapor pressure and temperature.[2] The magnetic VIC's are frequently in the 2-WLHS under normal ambient conditions. The c-axis repeat distance d is typically given by $d \approx 14.4$ Å for transition metal ion VIC's with 2-WLHS and $d \approx 14.9$ Å for rare-earth metal ion VIC's with 2-WLHS. Because of the large c-axis repeat distance, the magnetic VIC's may provide the model system for studying two-dimensional (2D) magnetism.

In our research we study the magnetic properties of magnetic VIC's with 0-WLHS and 1-WLHS from dc and ac magnetic susceptibility (Quantum Design, SQUID magnetometer).[3-9] The magnetic phase transition of these systems is expected to occur for the 0-and 1-WLHS, partly because of the decrease of c-axis repeat distance (0- and 1-WLHS) and the change of intraplanar interactions due to the water layers (1-WLHS). The exchange interaction between magnetic spins may be of the type of superexchange interaction via O^{2-} ions for the 1-WLHS where the water molecules and cations lie in the same layer. Like GIC's these systems may provide model

systems for studying the magnetic phase transition of 2D spin systems: 2D spin ordering mechanism and crossover behavior from 3D to 2D. It is of great importance to understand how the competition between various kinds of interactions such as interplanar and intraplanar interactions affect the magnetic properties of magnetic VICs. Here we present our results on the magnetic properties of the magnetic VIC's, Ni-VIC, Co-VIC, and rare-earth metal VIC's.

II.   Our Studies on magnetic VIC's

A.   Rare-Earth metal-VIC's[7]

The structural and magnetic properties of vermiculite intercalation compounds with 2-water layer hydration state (WLHS) having Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} ions in the interlamellar space between the host silicate layers, have been studied by means of $(00L)$ x-ray scattering, dc magnetic susceptibility, and thermogravimetric measurements. The intercalate layer sandwiched between two water layers consists of u cations and w water molecules per unit rectangular cell of $(a \times b)$: $u = 0.5 - 0.69$, $w = 0 - 4.0$. The c-axis
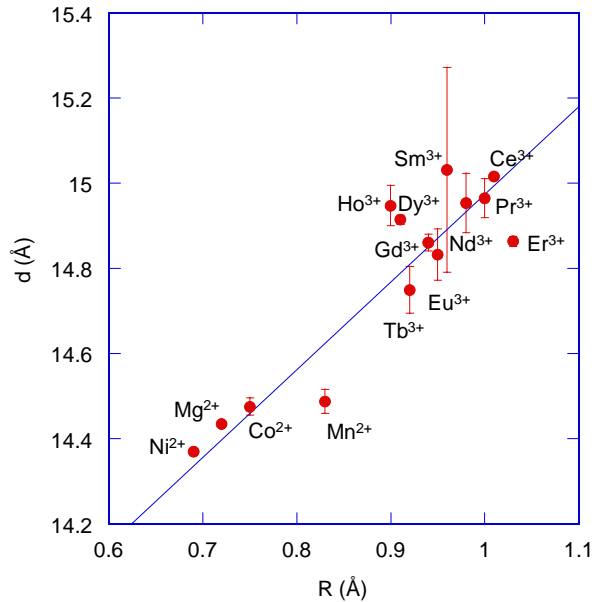

Fig. 1 c-axis repeat distance d (Å) vs ionic radius R (Å) for rare-earth metal-ion VIC's and transition-metal-ion VIC's with 2-WLHS. The solid line is a guide to the eye: $d = 12.98 + 2R$ [Ref. 7].

repeat distance is found to be roughly proportional to ionic radius, giving an indirect evidence for the strong rigidity of the host silicate layers. The magnetic susceptibility of these compounds shows a Curie-Weiss behavior. The Curie-Weiss temperature Θ for Ce^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+} is described by $\Theta = -1.58\ J(J + 1)$ [K], while Θ for Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} is described by $\Theta = 0.93\ (g_J - 1)^2\ J(J + 1)$ [K]. The Eu^{3+} VIC shows a Van Vleck susceptibility in the temperature range between 50 K and 300 K.

B.   Ni VIC[8]

Ni vermiculite intercalation compound (VIC) magnetically behaves like a quasi-2D Ising-like site-random ferromagnet on the triangular lattice sites, with weak antiferromagnetic interplanar interactions. The magnetic properties of Ni VIC have been studied using SQUID DC magnetization and SQUID AC magnetic susceptibility measurements. The 2D ferromagnetic short range order of Ni^{2+} spins starts to grow below 45 K. A partially disordered
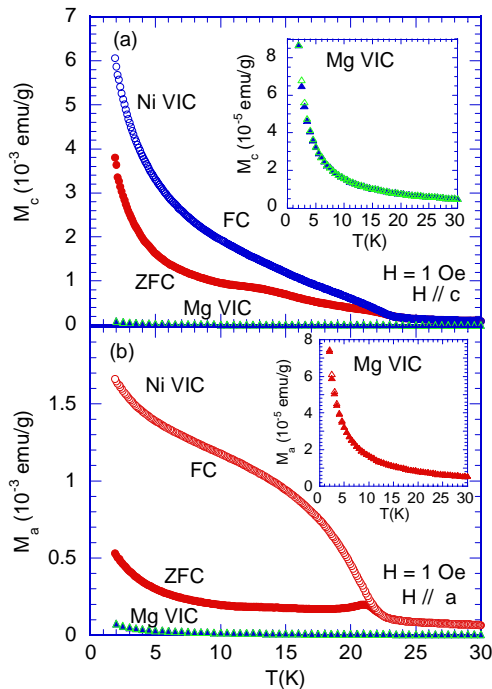

Fig. 2 T dependence of M_{FC} (○) and M_{ZFC} (●) for Ni VIC. $H = 1$ Oe. (a) $H // c$. (b) $H // a$. The corresponding data of M_{FC} (Δ) and M_{ZFC} (▲) for Mg VIC with two-WLHS ae also shown in the insets. $H = 1$ Oe. (a) $H // c$. (b) $H // a$ [Ref. 8].

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antiferromagnetic phase is established below T_N (= 21.0 K), where 2D ferromagnetic Ni clusters are antiferromagnetically coupled along the c axis. The dispersion χ'_{cc} along the c axis shows a peak around 2 – 3 K, shifting to the low temperature side with increasing the AC frequency. The temperature dependence of the corresponding average relaxation time is well described by a generalized Arrhenius law. The system may be formed of disordered antiferromagnetic clusters, exhibiting a superparamagnetic behavior.
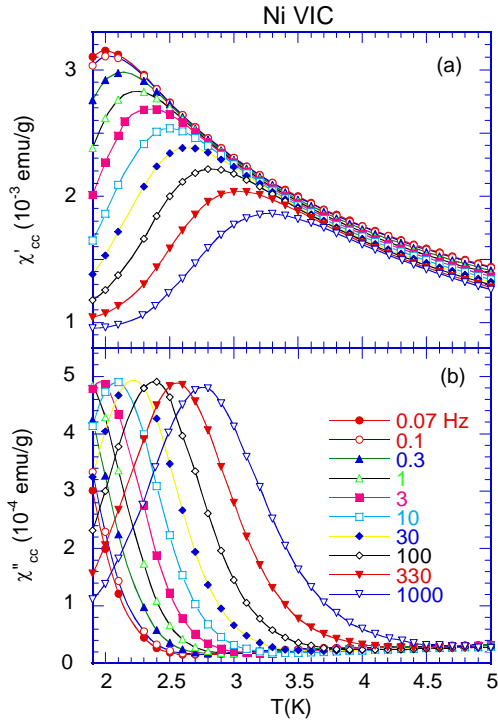

Fig. 3 T dependence of (a) χ'_{cc} and (b) χ''_{cc} for Ni VIC at various f (0.07 $\leq f \leq$ 1000 Hz). h = 2 Oe. h // c. H = 0. The solid lines are guides to the eyes [Ref. 8].

C. Co-VIC[9]

A Co vermiculite intercalation compound (VIC) magnetically behaves like an Ising-like Heisenberg antiferromagnet on the triangular lattice sites. This compound undergoes magnetic phase transitions at T_{N1} (= 16.3 K) and T_{N2} (= 10.7 K), and shows magnetic anomalies at T_{p1} (= 7.5 K), T_{p2} (= 5.9 K), and T_{p3} ($\approx$ 3 K). The c-axis spin order and the in-plane spin order occur at T_{N1} and T_{N2}, respectively. The magnetic phase diagram for H//c consists of four phases whose
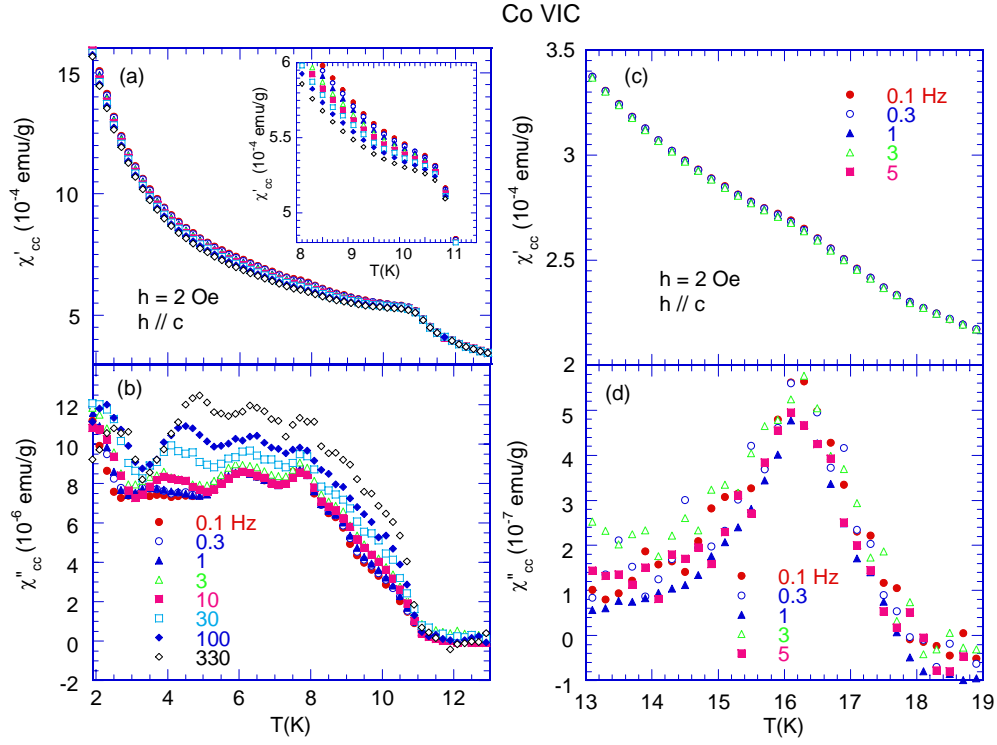
Fig. 4 *T* dependence of (a) χ'_{cc} and (b) χ''_{cc} for a Co VIC at various *f* (1.9 ≤ *T* ≤ 13 K). *h* = 2 Oe. *h* // *c*. *H* = 0. The detail of χ'_{cc} vs *T* around T_{N2} is shown in the inset. *T* dependence of (c) χ'_{cc} and (d) χ''_{cc} for a Co VIC at various *f* (13 ≤ *T* ≤ 19 K) [Ref. 9].

boundaries meet at a multicritical point (T_m ≈ 12 K, H_m ≈ 25 kOe). The freedom of rotation around an axis perpendicular to the spin plane where three sublattice magnetization vectors lie, would be frozen out below T_{p1} or T_{p2}. A superparamagnetic behavior of Arrhenius-type is observed around T_{p3}.

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