Magnetic Studies of Manganese Oxide Octahedral Molecular Sieves: A New Class of Spin Glasses

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Ac and dc magnetic susceptibility measurements of octahedral molecular sieves (OMS) of mixed-valent manganese oxide composition such as $(Mg^{2+}_{0.98-1.35}Mn^{2+}_{1.89-1.94}Mn^{4+}_{4.38-4.54})O_{12}\cdot 4.47-4.55H_2O$ for synthetic todorokite and KMn_8O_{16} for synthetic cryptomelane are reported here. Data for temperature and frequency dependence of the real components of the ac susceptibility suggest that synthetic cryptomelane (K-OMS-2) materials are spin glasses having a typical $T_f(\omega)$ dependence. The imaginary components of the ac susceptibility at various frequencies also show behavior that is typical of spin glass systems. Zero-field-cooled and field-cooled dc magnetization data as a function of temperature exhibit irreversibility, again consistent with the spin glass assignment for synthetic cryptomelane. Synthetic todorokite having a 3 × 3 MnO_6 octahedral tunnel structure does not appear to be a true spin glass.

Introduction

Molecular design of inorganic systems such as oxides has been the focus of several laboratories in recent years.[1-3] Physical and chemical properties of such systems may be dependent on the specific methods of preparation and synthetic precursors.[4] Several synthetic methods have been used to control properties such as sol–gel,[5] chemical vapor deposition,[6] hydrothermal alteration,[7] and other methods.[8]

Mixed-valent compounds are fundamentally of interest as regards transport of electrons in chemical, physical, and biological systems.[9] Several multinuclear manganese enzymes and model complexes have been under investigation, such as manganese catalases and photosynthetic water oxidases.[10-12] Magnetic studies of such systems have identified both antiferromagnetic and ferromagnetic materials with the hope of relating magnetic behavior to structural properties.

Molecular sieves are microporous materials having pores and dimensions on the order of molecular materials.[13] Aluminosilicate sieves or zeolites have been studied by numerous research groups for several decades. Zeolites have tetrahedrally coordinated Al^{3+} and Si^{4+} oxide framework structures. There has been considerable interest in substituting other ions for Al^{3+} and Si^{4+} in such materials.[14]

Mixed-valent manganese oxide octahedral molecular sieves (OMS) have recently been the subject of several reports from our laboratories.[15-16] Such materials consist of edge- and corner-shared octahedra that form a tunnel structure. When two octahedra are bound on each side of a tunnel, the hollandite or cryptomelane structure results, which we have labeled OMS-2. If there are three octahedra on each side of the tunnel, the todorokite or OMS-1 structure is formed. A related phase is the layered birnessite structure which has an octahedral layer (OL-1) structure and is a synthetic precursor to OMS-1.[15,16] The structures of these materials are shown in Figure 1.

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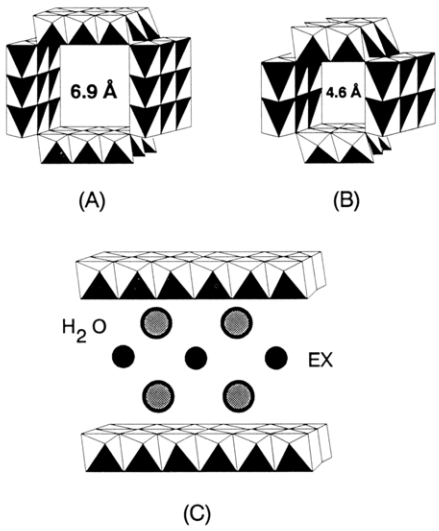

Figure 1. Structures of (a) OMS-1, (b) OMS-2, and (c) OL-1; EX = exchangeable cations.

These OMS materials have interesting structural, catalytic, electrical, and adsorptive properties.[15,16] Recent electrochemical studies[17] have shown that the OMS materials have ion-exchange properties, different pore sizes, and electrical conductivities.[18] The nature of electron transport in such materials is not well understood; however, some high-temperature conductivity measurements suggest that their electrical conductivities are not Nernstian in a classical sense.[15,16]

Electron paramagnetic resonance and titration data for such systems suggest that OMS-1 has Mn^{2+} ions present and has a lower average oxidation state than cryptomelane systems (OMS-2) which are predominantly Mn^{4+} and Mn^{3+} ions.[15,16] Electrical conductivity measurements[18] suggest that OMS-2 is a better conductor than OMS-1 (2 orders of magnitude); however, both have conductivities of the magnitude commonly observed for semiconductor materials.

With these structural, electronic, electrical, and spectroscopic data in mind, it is important to consider the magnetic properties[19] of these materials. Such magnetic properties might be expected to be complicated by the small particle sizes (<0.6 μm) of OMS-1 and OMS-2 crystals which are desirable for adsorption and catalysis.

For example, the size and shape of small clusters of Co trapped in zeolites has been found to be directly related to catalytic activity in reactions of cyclopropane and H_2. The sizes and particular shapes of ferromagnetic domains have been observed in such systems with variable-temperature ferromagnetic resonance methods[20] and spin echo nuclear magnetic resonance[21] methods.

In addition, the good conductivity in such systems implies delocalization of electron density, whereas magnetic properties can be significant when electrons are localized.[22] Delocalized systems may result in weak magnetism such as Pauli paramagnetism, whereas localization of electrons leads to local moment magnetization.

The objective of this research was to study the magnetic properties of OMS systems. Both dc and ac magnetic studies at variable temperature and frequency have been carried out. Results of these studies suggest that OMS-2 materials have properties of spin glass systems.

Experimental Section

Preparation of Materials. Synthetic todorokite (OMS-1) was prepared according to literature procedures.[15,16] In general, $Mn(OH)_2$ sols were formed by mixing NaOH and $MnCl_2$ solutions. The $Mn(OH)_2$ sols were then added to $Mg(MnO_4)_2$ solutions while stirring at pH 13.8. After resultant suspensions were aged for 8 days, a layered material resulted which was ion-exchanged with Mg^{2+} and then autoclaved at 155–170 °C for 10–40 h. The Mg^{2+} form of this material was used for all magnetic studies reported here. This material will be designated Mg–OMS-1.

The K^+ form of OMS-2 [K–OMS-2] was prepared by using literature procedures.[17,23] In general, solutions of $KMnO_4$ and Mn^{2+} have been refluxed in HNO_3 at 120 °C and the resultant precipitates were washed in distilled deionized water (DDW), filtered, and dried. A typical synthesis involves adding 5.89 g of $KMnO_4$ in 100 mL of H_2O to a solution of 8.8 g of $MnSO_4 \cdot H_2O$ in 30 mL of H_2O) and 3 mL of concentrated HNO_3. The mixture was refluxed for 24 h, then filtered, washed with DDW, and dried at 120 °C in air. In some cases, materials were loaded into stainless steel autoclaves and heated to 100 °C for 24 h to enhance crystallinity and produce larger particle sizes. Hydrothermal processing can enhance the length of fibers of these materials from about 2000 to about 8000 Å. These materials have the cryptomelane structure and the composition KMn_8O_{16}.

Both Mg–OMS-1 and K–OMS-2 were characterized with X-ray powder diffraction, cyclic voltammetry, atomic absorption, inductively coupled plasma, electron paramagnetic resonance, differential scanning calorimetry, thermogravimetric analytical, and other methods as has been described previously.[15–17,23]

Magnetic Studies. Mg–OMS-1 and K–OMS-2 as black powders were loaded into cylindrical Teflon sample holders. About 0.2-g samples were used for all studies. These materials are present in their hydrated forms.

Magnetic studies were done with a Lake Shore Cryotronics, Inc. Model 7000 ac susceptometer/dc magnetometer system operated between 4.2 and 325 K. An ac field amplitude between 0.00125 and 20 Oe root-mean-square was used for all experiments. Frequency measurements were done between 1 Hz and 10 kHz. A 0.1-T (1 kOe) dc magnetic field strength was used for field cooled magnetization experiments by using a 1-T superconducting magnet. An HP Vectra 386 computer with a 50M hard drive and ACS7000 software were used for all data collection and data analysis.

Results

Synthetic and characterization methods using X-ray powder diffraction, atomic absorption, inductively coupled plasma, electron paramagnetic resonance, electrochemistry, and other methods showed that pure Mg–OMS-1 and K–OMS-2 materials were prepared. These materials are crystalline, single phase, and mixed valent [$Mn^{2+/3+/4+}$ for Mg–OMS-1; Mn^{3+}/Mn^{4+} for K–OMS-2] and have particle sizes less than 0.6 μm.[15,16] Hydrothermal treatment enhances the lengths of the OMS-2 materials by about a factor of 4 with respect to reflux methods.[17,23]

A plot of ac susceptibility showing the real or in-phase component (χ') and the imaginary or out-of-phase component (χ'') as a function of temperature between 4.2 and 100 K is shown in Figure 2. These susceptibilities are presented in terms of mass susceptibility (emu/g, cgs units).

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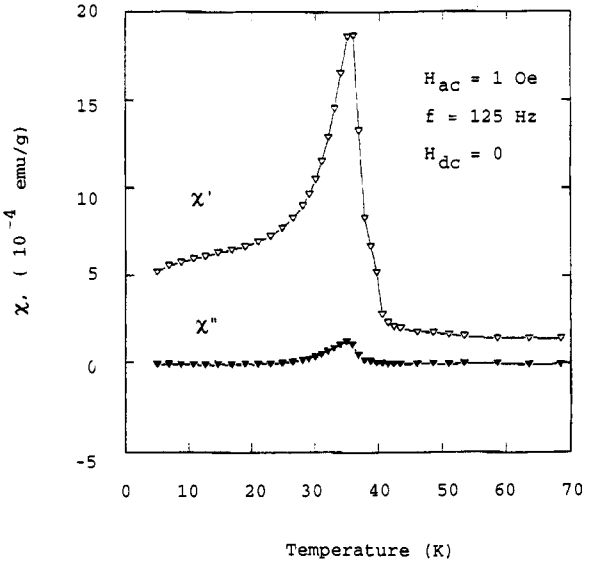

Figure 2. Plot of ac susceptibility as a function of temperature for Mg–OMS-1. H_{ac} = 1 Oe, ν = 125 Hz, H_{dc} = 0.

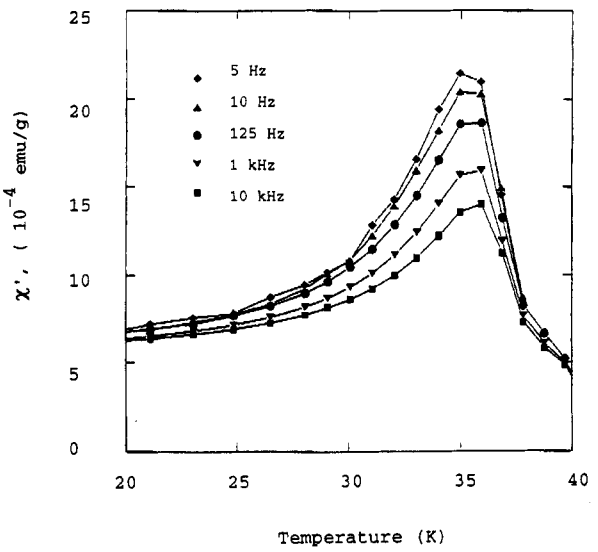

Figure 3. Plot of χ' versus temperature at various Frequencies for Mg–OMS-1. H_{ac} = 1 Oe, H_{dc} = 0.

Note that χ' reaches a maximum near 35 K and has susceptibilities above and below 35 K that are about the same. The temperature dependence of χ'' as shown in Figure 2 is very similar to that of χ'.

Figure 3 shows the temperature and frequency dependences of the real ac susceptibility component χ'. For these data, the ac magnetic field strength H_{ac} was set at 1 Oe RMS and the dc magnetic field strength H_{dc} was 0. The frequency was varied between 5 Hz and 10 kHz. All of the χ' versus temperature plots are maximized at 35 K.

Figure 4 shows the temperature and frequency dependences of the imaginary ac susceptibility component χ''. For these data, the ac magnetic field strength H_{ac} was set at 1 Oe RMS and the dc magnetic field strength H_{dc} was 0. The frequency was varied between 5 Hz and 10 kHz. Only the 10-Hz, 125-Hz, 1-kHz, and 10-kHz data are plotted since the 5-Hz data are very weak and essentially noise. All of the χ'' versus temperature plots are maximized at 35 K.

Data of Figure 5 show a comparison of zero-field-cooled (ZFC) dc magnetization and field-cooled magnetization data between 5 and 50 K. Note that above 35 K both the ZFC and FC magnetization data are virtually identical

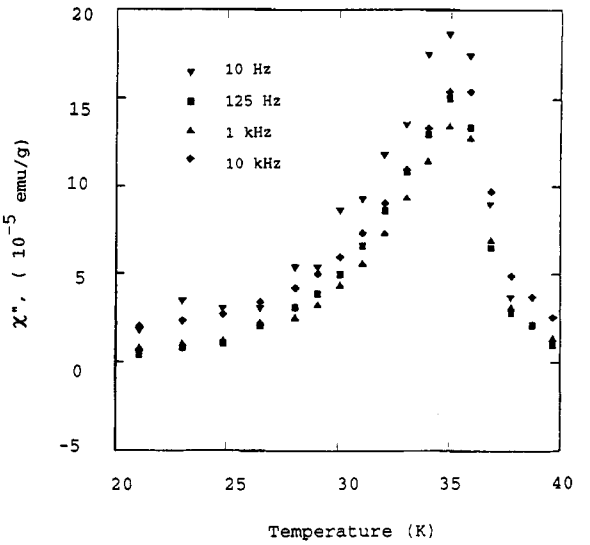

Figure 4. Plot of χ'' versus temperature at various Frequencies for Mg–OMS-1. H_{ac} = 1 Oe, H_{dc} = 0.

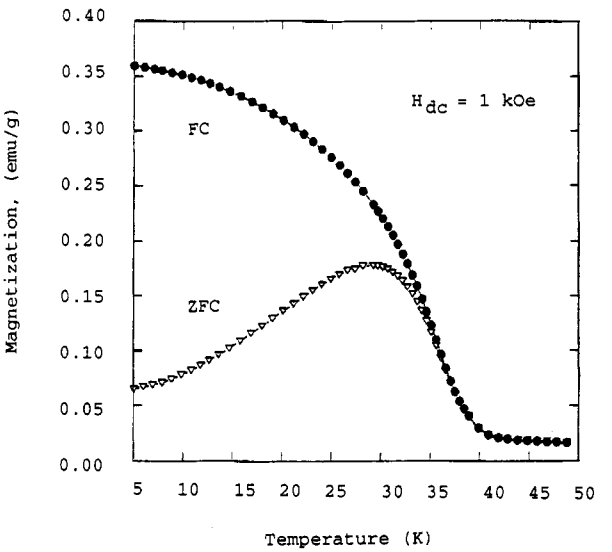

Figure 5. Plot of dc magnetization versus temperature for Mg–OMS-1. H_{dc} = 1 kOe.

but that they diverge at low temperature. The field-cooled experiments were done with a 1-kOe magnetic field strength.

A set of experiments similar to those of Figures 2–5 for Mg–OMS-1 were done for K–OMS-2 as shown in Figures 6–9. Figure 6 shows a plot of χ' and $10\chi''$ as a function of temperature. In this case, χ' has a maximum near 13 K and $10\chi''$ has a maximum near 11 K. The real and imaginary components of the ac magnetization are not the same above and below these peak maxima as was the case in Figure 2. For these data, H_{ac} was 2 Oe and the frequency was 125 Hz.

A plot of χ' versus temperature at various frequencies is shown in Figure 7 for K–OMS-2. The data are maximized near 12–13 K. Note that the 10- and 125-Hz data are shifted toward lower temperatures than the data collected at 1 and 10 kHz. The 1- and 10-kHz data were collected at an H_{ac} magnetic field strength of 1 Oe RMS, whereas the 10- and 125-Hz data were collected at 8 and 2 Oe RMS, respectively.

A plot of χ'' versus temperature at various frequencies is shown in Figure 8 for K–OMS-2. The 125-Hz, 1 kHz, and 10-kHz data are all maximized near 11 K. Data collected at 10 Hz are noisy and are not shown here.

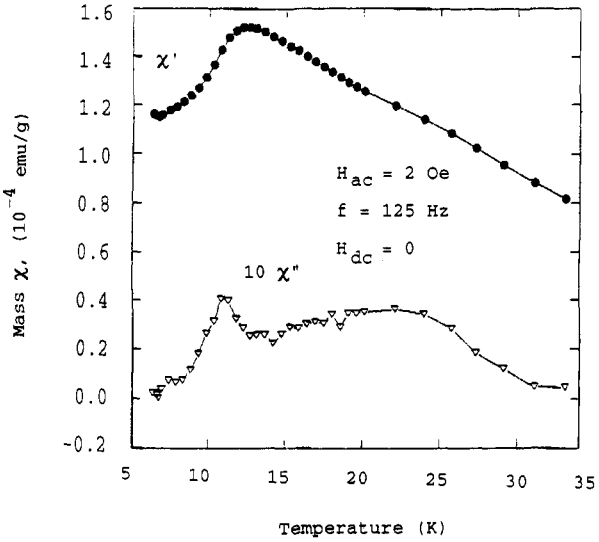

Figure 6. Plot of ac susceptibility as a function of temperature for K–OMS-2. H_{ac} = 1 Oe, ν = 125 Hz, H_{dc} = 0.

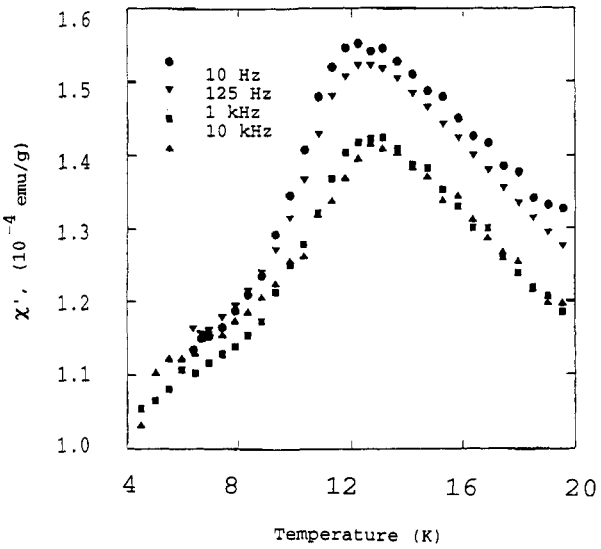

Figure 7. Plot of χ' versus temperature at various Frequencies for K–OMS-2. H_{ac} = 1 Oe, H_{dc} = 0.

Figure 9 shows zero-field cooled and field-cooled dc magnetization data versus temperature where H_{dc} was set at 1 kOe. Even at temperatures as high as 22 K, the ZFC and FC data are divergent.

Discussion

Magnetic Susceptibility. Ac susceptometry involves application of an alternating magnetic field to a sample with an ac current through a coil. Two oppositely wound secondary coils are connected in series in order to measure variations in magnetic flux created by the presence of the sample in one of the secondary coils. Phase-sensitive detection is used that generates output voltages that are proportional to the susceptibility of the sample. The susceptibility depends on a number of factors including the volume of the sample, the frequency of the ac field and the magnetic field.[24]

The real or in-phase component (χ') of the ac susceptibility (χ_{ac}) and the imaginary or out-of-phase component (χ'') are related to the complex susceptibility by the

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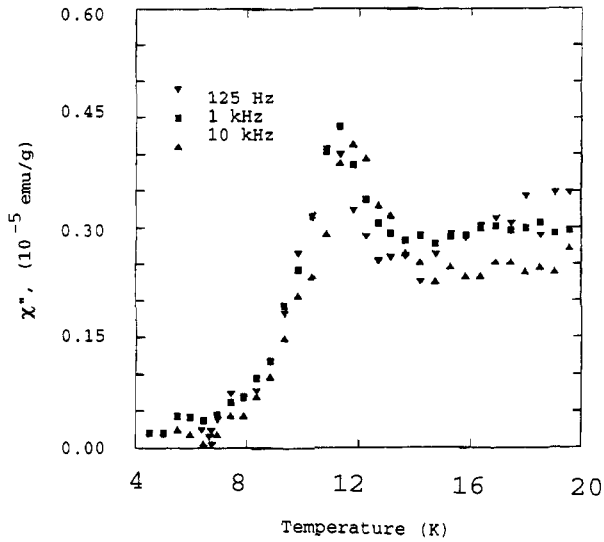

Figure 8. Plot of χ'' versus temperature at various Frequencies for K–OMS-2. H_{ac} = 1 Oe, H_{dc} = 0.

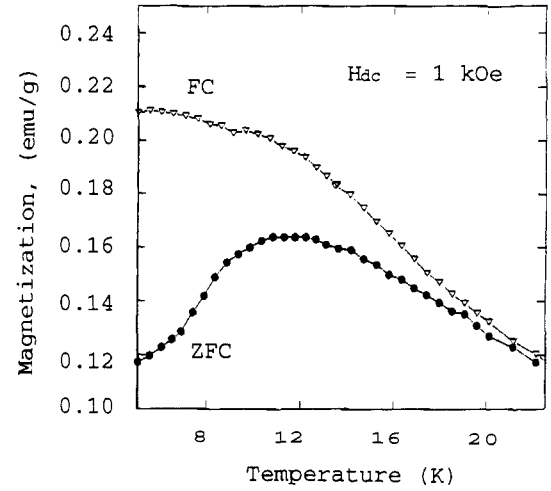

Figure 9. Plot of dc magnetization versus temperature for K–OMS-2. H_{dc} = 1 kOe.

relationship of eq 1. The magnetic susceptibility (χ) is a

$$\chi_{ac} = \chi' - i\chi'' \quad (1)$$

measure of the degree of magnetism of a material. The imaginary component χ'' represents a measure of dissipative losses in that material. Time-dependent and relaxation processes will give rise to nonzero χ'' values. Nonlinearities and hysteresis in dc magnetic behavior will also generate χ'' components.[25]

Magnetic Properties of OMS Materials. Data of Figure 2 for Mg–OMS-1 definitively show that there are both real and imaginary components of the susceptibility. The reason χ' has different values above and below 35 K is not understood. There is clearly a sharp phase transition at 35 K. The temperature at which this phase change occurs is known as the freezing temperature and is labeled T_f.

The plots of the real components of the susceptibility as a function of temperature for various frequencies for Mg–OMS-1 of Figure 1 show behavior which is charac-

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terized by a decrease in χ' with increasing frequency but with no major shift in T_f. Note that both the maxima in χ' and χ'' are frequency dependent and that the temperature of the maxima for K–OMS-2 are not coincident [$T(\chi'_{max}) > T(\chi''_{max})$] (Figures 6–8) in contrast to the magnetic data for OMS-1 where $T(\chi'_{max}) = T(\chi''_{max})$ as shown in Figures 2–4.

Spin Glasses. Spin glasses are materials that are characterized by a peak in the magnetic susceptibility as a function of temperature which is not due to ferromagnetic or antiferromagnetic transitions. Specific heat, electrical conductivity, or structural data do not show similar singularities at T_f.[26]

At temperatures below T_f, spins may cluster together as domains and are trapped in highly reversible metastable states. Above T_f, such materials behave as randomly positioned free rotating spins or Curie–Weiss paramagnets which may cluster. Near T_f, spin interactions become effective over a larger range than at high temperature.[26]

Figures 5 and 9 illustrate divergence of zero-field-cooled and field-cooled dc magnetization data for Mg–OMS-1 and K–OMS-2, respectively. This divergence below T_f shows a clear irreversibility in magnetic character. The apparent T_f is dependent on the magnitude of the magnetic field.

Exact criteria for spin glass behavior are that both the maxima in χ' and χ'' are frequency dependent and that the temperature of the maxima are not coincident.[26,27] Comparison of data for Mg–OMS-1 in Figures 2–4 and data for K–OMS-2 in Figures 6–8 therefore suggest that only K–OMS-2 is a spin glass material.

The facts that the K–OMS-2 systems show dynamic effects (dependence of ac susceptibility on ν) and a field dependence (field-cooling effects) suggest that these systems are spin glasses which do not show phase transitions, i.e., they are not simple ordered magnetic systems. The different magnetic properties of Mg–OMS-1 with respect to K–OMS-2 may be attributed to weak or dilute magnetic systems such as ferromagnets and weak ferromagnets in low applied magnetic fields and dilute antiferromagnets.[26,27]

Differences in magnetic properties of Mg–OMS-1 and K–OMS-2 may be related to a variety of chemical and physical properties such as structure, composition, and valence. It has not yet been possible to prepare pure K–OMS-1 and Mg–OMS-2 materials since it is believed that such cations act as templates during crystallization[15–17] and that OMS-1 prefers divalent cations, whereas OMS-2 prefers monovalent cations.[15–17,23]

The average oxidation state of manganese in such materials can be varied somewhat and at least partial substitution of divalent cations such as Cu^{2+} in both OMS-1 (for Mn^{2+}) and OMS-2 (for K^+) can be done.[15,17,23] Such substitutions have not as yet led to changes in magnetic properties, suggesting that exchangeable cation content does not markedly influence magnetic phenomena.

Magnetic data for OL-1 show a much reduced frequency dependence with respect to either Mg–OMS-1 or K–OMS-2. There also appear to be no imaginary components. The average Mn valence in OL-1 is about 3.6 in comparison to 3.5 for Mg–OMS-1 and 3.9 for K–OMS-2.[15,17,23] Preliminary magnetic data for divalent ions exchanged into OL-1 show no major changes in magnetic properties. All of the above observations might suggest that magnetic properties are quite dependent on the specific structure of the material. Further studies will need to be done to unravel the differences in magnetic properties of Mg–OMS-1, K–OMS-2, and OL-1.

Spin glass systems are a fascinating group of materials being theoretically investigated by several condensed matter physicists since similar properties have been observed for superparmagnets and high temperature superconductors.[26–29] Considerable efforts are being made in the area of theoretical investigations of spin glasses such as with mean-field theory.[26,30,31] K–OMS-2 materials are new classes of materials that may provide insight into the magnetic properties of such systems.

Conclusions

Microporous octahedral molecular sieves having the cryptomelane structure have been shown here to have properties of spin glasses. The behavior of both the real and imaginary components of ac susceptibility and the divergence in the dc magnetization of these materials are consistent with spin glass systems. Octahedral layered materials similar to birnessite and octahedral molecular sieves having the todorokite structure (OMS-1) do not appear to be spin glass materials. The combination of good electrical conductivity of K–OMS-2, Mg–OMS-1, and OL-1 coupled with interesting magnetic properties of OL and OMS materials is unusual.

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