RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 22 1 DECEMBER 1994-II

Titanium-III warwickites: A family of one-dimensional disordered magnetic systems

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(Received 8 July 1994)

We present x-ray, susceptibility, and magnetization (up to 18 T) measurements in the compound $MgTiOBO_3$, which forms in the structure known as warwickite. This structure is characterized by the presence of ribbons along the c axis where the metallic ions are located. This system is magnetic since the Ti ions are in the valence state Ti^{3+} with the electronic configuration $3d^1$. Its susceptibility has a temperature dependence, at low temperatures, given by $\chi(T) \propto T^{-\alpha}$, with the exponent $\alpha \approx 0.83$. The low-temperature behavior of the magnetization, as a function of field, is described by $m \propto H^{\gamma}$ with $\gamma \approx 1-\alpha$. These results, together with the x-ray measurements, allow us to identify this material as belonging to a family of inorganic, one-dimensional, disordered magnetic systems.

The discovery of high-temperature superconductivity in copper oxides has attracted much attention to low-dimensional, strongly correlated, electronic systems. In fact these are believed to be the essential ingredients responsible for the properties of these materials.[1] Also in the copper oxides the simple electronic configuration of the Cu^{2+} ion, with an unpaired spin, seems to play an important role.[1] Using as general guidelines, low-dimensional structures and strong correlations, we were led to search for materials containing transition elements, now in the beginning of the series, with low-dimensional structures and single unpaired spins. This search led us to synthetize a family of mixed borates known as *warwickites*.[2–7]

The warwickites were characterized and extensively studied from the structural point of view. A careful and systematic study of their crystallographic structure for different chemical compositions was made by Capponi *et al.*[5] To the best of our knowledge no magnetic studies were made in these systems in spite of the fact that some of them contain transition metals in magnetic configurations[2,5,8] and rare-earth elements.[5]

The materials we have synthetized have the general chemical composition $XYOBO_3$, where X stands for the alkaline-earth metals Mg or Ca and Y for the transition metals Sc or Ti. Since the boron ion is trivalent and the alkaline-earth metal divalent, the transition metal assumes, in the above chemical formula, the Y^{3+} configuration. In the compound $MgScOBO_3$ (Ref. 7) the Sc ion is in the electronic configuration $3d^0$ and therefore is nonmagnetic (see Table I). On the other hand, in $MgTiOBO_3$, the Ti ion is in the $3d^1$ magnetic configuration, with a single unpaired spin, which gives rise to magnetic behavior. As it will be seen below, the metallic ions in the warwickites are located along *ribbons* which ensure the low dimensionality of the interactions. We have then obtained a system which has the appealing combination of a low-dimensional structure and, as we have observed, strong correlations. Table I shows the transition metal ion configuration and respective crystal color for some warwickites. It is interesting to observe that for the system $Mg_{1.5}Ti_{0.5}OBO_3$, where part of the Ti is substituted by Mg, charge neutrality forces the Ti ions in a tetravalent, nonmagnetic configuration, changing the optical properties radically.

The crystalline structure of the warwickites is orthorhombic with sides a and b of the unitary cell measuring approximately 10 Å and the c side close to 3 Å (Table II). Since c is much less than a and b they were described by Moore and Araki[6] as members of the group 3*A* structure. The spatial group of symmetry is $V_h^{16}-Pnam$.[6]

The structure of the warwickites projected on the plane (001) is shown in Fig. 1.[7] We can observe in this figure parallelograms which were orthogonal sections of substructures, similar to ribbons, which extend indefinitely along the

TABLE I. Some warwickites with the valence and electronic configuration of the transition metal. The color of the crystals is determined by the oxidation state of the transition metal. PW stands for present work.

Compound	Valence	Configuration	Crystal color
$MgScOBO_3$	+3	Argon	Polished silicon [PW]
$CaScOBO_3$	+3	Argon	Polished silicon [PW]
$MgTiOBO_3$	+3	Argon $+3d^1$	Black [PW]
$Mg_{1.5}Ti_{0.5}OBO_3$	+4	Argon	Yellowish white [4]

TABLE II. Cell parameters of some warwickites. PW stands for present work.

Compound	*a* (Å)	*b* (Å)	*c* (Å)	Ref.
$MgScOBO_3$	9.490	9.422	3.218	[7]
$MgTiOBO_3$	9.186	9.337	3.028	[PW]
$Mg_{1.5}Ti_{0.5}OBO_3$	9.236	9.444	3.001	[4]
$(Mg,Fe)_{1.5}Ti_{0.5}OBO_3$	9.20	9.45	3.01	[2]

c axis. Such ribbons are formed by oxygen octahedra packed in the hexagonal form and sharing edges in such a way that three of their vertices lie on each one of the larger faces of the ribbons. These octahedra give rise to four columns, along the ribbons, and their centers define two types of equivalent crystallographic sites: those on the border (sites 2) and those on the center of the ribbons (sites 1) (see Fig. 1). These sites form a section of a triangular lattice and are randomly occupied by the alkaline-earth and transition metal ions. In fact in the warwickites $MgScOBO_3$, according to Norrestam,[7] sites 1 have 76% of the transition metal ions and 24% of the alkaline-earth ones. Sites 2 have the opposite occupancy. The boron ions are bound to three oxygen ions of different ribbons ensuring, in this way, the rigidity of the crystal. An important and attractive property of the warwickites is the flexibility of this structure which allows for different components and a large range of chemical compositions.[5]

The crystals of $Mg_{1-x}Ti_{1+x}OBO_3$, with $x=0$ and 0.1, on which we made the studies reported here, were obtained from a reaction of the oxides MgO, TiO, TiO_2, and B_2O_3 in argon atmosphere at 1200 °C. The warwickite crystals were black, as expected from the oxidation state of the Ti, in the form of needles about 50 μm long due to the smallness of the *c*-axis side. This reaction yielded also, as a by-product, to the formation of the compound $MgTi_2O_5$ as may be seen on the x-ray spectrum shown in Fig. 2 for the $x=0$ material.

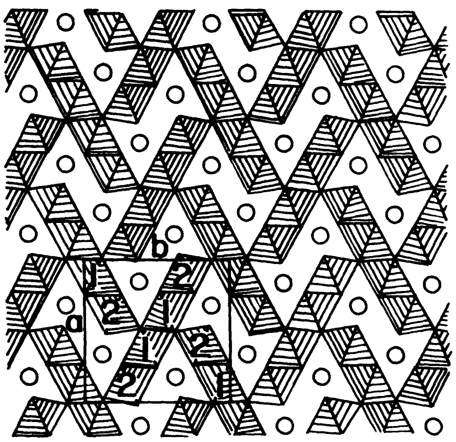

FIG. 1. The structure of the warwickites projected in the plane (001). Shown are the sides *a* and *b* of the unitary cell, the sections of the ribbons, sites 1 and 2 where the metallic ions are located as well as the boron ions (○) (adapted from Ref. 7).

The sharpness of the warwickite spectral lines confirms the existence of well-formed crystals as anticipated by an examination of the products of the reaction in the microscope. Fortunately the unwanted $MgTi_2O_5$ is diamagnetic, since the Ti is tetravalent in this compound and gives no contribution to the magnetic measurements we describe now. The axis lengths we have found for $MgTiOBO_3$ are very close to those reported by Blum and Bozon.[3]

We discuss now the magnetic susceptibility measurements in the system $Mg_{1-x}Ti_{1+x}OBO_3$. They were done using commerical equipment to obtain data from 100 to 1.8 K at a frequency of 125 Hz in an ac field of 10 Oe. The results are shown in Fig. 3 for two different compositions $x=0$ and $x=0.1$. The susceptibilities $\chi(T)$ are temperature independent, in both cases, down to approximately $T=30$ K, where they start to rise with decreasing temperature. This rise is

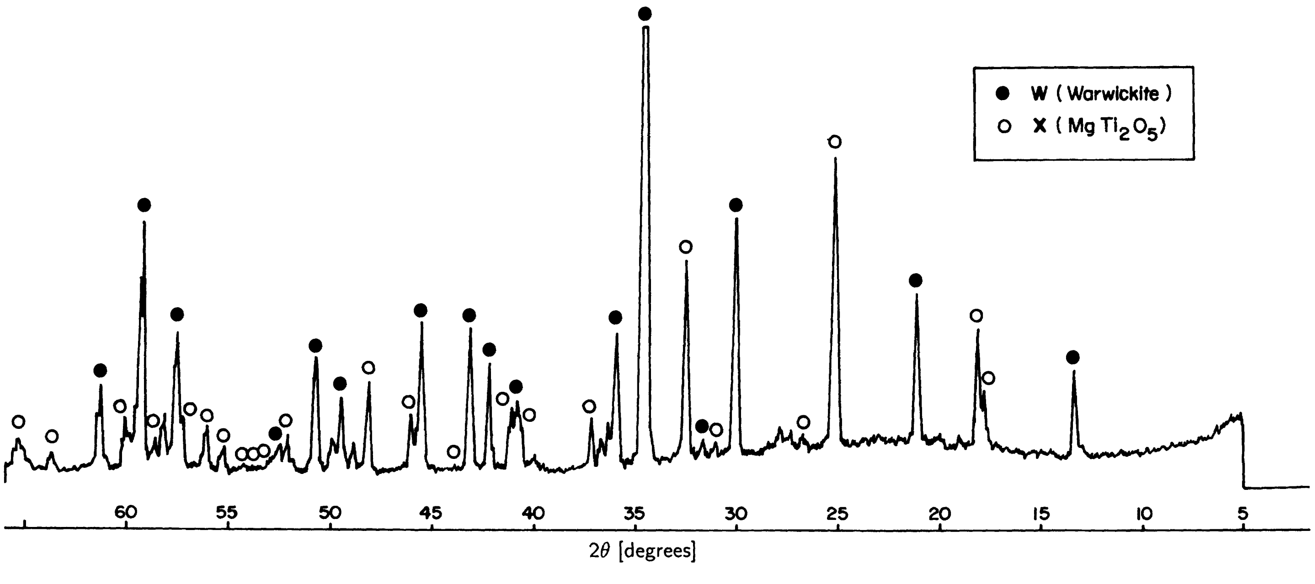

FIG. 2. X-ray diffractogram, under Cu $K\alpha_1$ radiation, of the material prepared as described in the text. We can see the peaks associated with the warwickites and also those of $MgTi_2O_5$ which appears as a by-product of the reaction. The latter belongs to the armalcolite or pseudobrookite group [Nat. Bur. Stand. (US) Monogr. **25**, 21 (1984)].

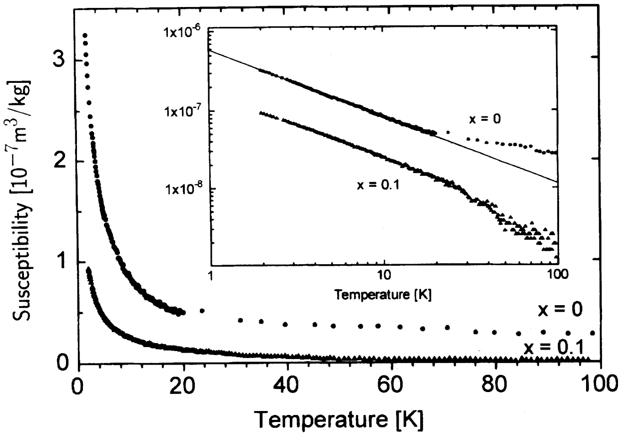

FIG. 3. ac susceptibilities of the $Mg_{1-x}Ti_{1+x}OBO_4$ warwickites as a function of temperature for $x=0$ and $x=0.1$. The inset shows the power law behavior of the low-temperature susceptibilities of both samples, characterized by a *single* exponent α ($\alpha \approx 0.83$).

very well described by a power law, i.e., $\chi(T) \propto T^{-\alpha}$ with the exponent $\alpha \approx 0.83$, independent of the concentration of Ti, as is clearly shown by the log-log plot in the inset of Fig. 3.

A similar temperature dependence of the magnetic susceptibility has been observed previously in one-dimensional organic compounds based on the *TCNQ* molecule.[9,10] It is generally associated with a Heisenberg chain of spins $S=1/2$ with random antiferromagnetic interactions described by the Hamiltonian[11,12]

$$\mathcal{H}=\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j, \tag{1}$$

where the antiferromagnetic interactions J_{ij}, in our case between the Ti ions, are distributed according to a probability distribution $P(J_{ij})$. The random Heisenberg antiferromagnetic chain has been studied by different techniques.[11–13] The general result which emerges from these theoretical calculations is that, at sufficiently low temperatures, the thermodynamic properties of the system are given by

$$\begin{aligned} \chi &= AT^{-\alpha}, \\ C &= BT^{1-\alpha}, \end{aligned} \tag{2}$$

where χ is the uniform susceptibility and C the magnetic contribution to the specific heat.[14] For sufficiently strong uniform magnetic fields H, i.e., for $k_BT \ll g\mu_BH \ll J$, where J is the cutoff of $P(J_{ij})$, the magnetization behaves as[11]

$$m \propto H^{1-\alpha}. \tag{3}$$

Within the renormalization group, the results given by Eq. (2) turn out to be independent of the particular form of the probability distribution $P(J_{ij})$. The exponent α has a weak temperature dependence with the scale determined by the cutoff of the probability distribution of the interactions.[11,12]

In $MgTiOBO_3$ we find that, as in the case of the organic materials based on *TCNQ*, a temperature-independent exponent α gives a very good description of the experimental results. Furthermore, this exponent is independent of the concentration of Ti, contrary to the amplitude A of Eq. (2) (Fig. 3), in agreement with the property of *quasiuniversality* which emerges from the renormalization group calculations.[11,12,10] In the organic materials susceptibility measurements yield exponents α which range from 0.79 to 0.86 depending, although weakly, on the degree of disorder.[10]

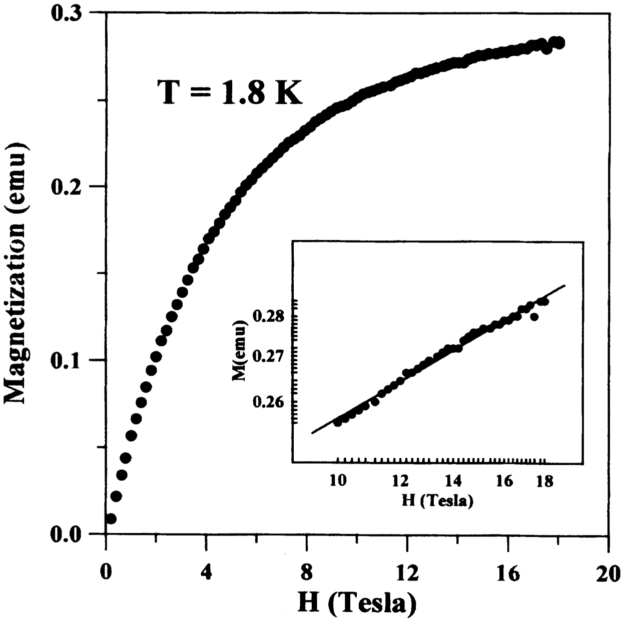

FIG. 4. Magnetization as a function of magnetic field for $MgTiOBO_3$ at 1.8 K. The inset, in log-log scale, shows the power law behavior of the $m(H)$ data, for sufficiently strong magnetic fields. The straight line is a fit by the law $m(H) \propto H^{1-\alpha}$, with $1-\alpha \approx 0.2$.

The fact that the ribbons have a finite width is irrelevant from the point of view of critical behavior, as soon as the correlation length becomes larger than this width. However, the triangular sites in the ribbon, randomly occupied by Ti ions, can give rise to frustration and incommensurabilities which do not occur for a strictly one-dimensional system.

In order to provide unambiguous evidence for random exchange Heisenberg antiferromagnetic chain (REHAC) behavior in the magnetic warwickites, high-field (up to 18 T) magnetization measurements were performed at the National High Magnetic Field Laboratory–Los Alamos Facility, at Los Alamos National Laboratory. The experiments were done in a 20 T superconducting magnet, at fixed temperatures of 1.8 and 2.88 K. The magnetic field was ramped up and down to search for possible signs of hysteresis, at a rate of 0.5 T per minute. A powdered sample of $MgTiOBO_3$ with a total mass of 17 mg was assembled in the VSM sample holder operated at 80 Hz. We find no signs of hysteresis upon reducing H and a magnetization that has a slightly higher initial slope for the lower temperatures. For both temperatures the magnetization as a function of the magnetic field follows Eq. (3), with the same exponent $\gamma \approx 1-\alpha \approx 0.2$ for fields greater than approximately 10 T (see Fig. 4). Both measurements do not indicate a saturation of m with H. Even higher-field measurements are planned for the near future. To the best of our knowledge, this is the first time that the magnetic behavior shown in Figs. 3 and 4 has been found in inorganic, one-dimensional, materials.

We have presented results of x-ray, susceptibility, and magnetization measurements on Ti warwickites. These results allow us to identify these materials as belonging to a new family of inorganic, one-dimensional, magnetic systems. The lack of saturation of the susceptibility down to the lowest temperatures shows that the ribbons which contain the transition metals have a negligible interaction and these magnetic warwickites are almost ideal one-dimensional disordered magnetic systems. These materials provide model systems which can be described by the one-dimensional Heisenberg or Hubbard Hamiltonians with disorder. For the latter, the case of different band fillings may be also realized. Different from the case of the organic REHAC materials we have here the possibility of varying the spins of the magnetic elements in the chain. Work is now in progress to study the magnetic and transport properties of the warwickites with different kinds of doping and magnetic constituents.

We would like to thank the Brazilian agencies CNPq and FINEP for partial financial support. We also thank FERMAVI Ind.e Com., SP-Brasil for providing material support in the preparation of the samples. M.A.C. thanks M. Novak for useful discussions. Work at the National High Magnetic Field Laboratory (NHMFL) was performed under the auspices of the National Science Foundation, Florida State University, and the U.S. Department of Energy. Special thanks go to Professor Milton Torikachvili for help with the construction of the VSM apparatus at the NHMFL–Los Alamos Facility.

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