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THE STRUCTURE OF $HoMn_2O_5$ FORMED BY TWO-LAYER PEROVSKITE BLOCS $[Mn_{0.5}O_{2.5}]$ SEPARATED BY HoMn ROCK-SALT LAYERS

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The magnetic properties of layered $HoMn_2O_5$ monocrystals were studied in the temperature interval 4.2–150 K and in magnetic fields with the induction of up to 15 T. It was established that at room temperature the crystals have orthorhombic structure and possess ferromagnetic properties. At temperatures lower than 18 K crystals undergo phase transition and become antiferromagnetics with tetragonal structure.

Key words: layered perovskites, colossal magnetoresistance.

PACS number(s): 71.70 Gm

I. INTRODUCTION

The two-layered perovskite-like manganate $HoMn_2O_5$ has become the subject of intense interest and has been widely investigated due to its colossal magnetoresistance (CMR) and a variety of fascinating physical properties. $HoMn_2O_5$ is a typical quasi-two-dimensional layered-perovskite material. Quasi-two-dimensional layered-perovskites, and especially the layered perovskite-like manganates $(A,B)_{x+1}Mn_xO_{3x+1}$ (A is a rare earth trivalent ion and B is a divalent cation) have been extensively studied in recent years [1–3]. The transport properties of manganite perovskites with CMR are attributed to strong interactions among charge, spin, and lattice degrees of freedom [4–6]. Reducing the dimensionality of these perovskites (by constraining the lattice degrees of freedom and by enhancing the amplitude of charge magnetic fluctuations in the critical region above the insulator–metal transition) and studying their behaviour in layered phases can help elucidate these interactions. The competition between charge, lattice, and spin degrees of freedom can be delicately balanced to form materials where electrons localize on alternate transition metal site on a lattice. The so-called charge ordered (CO) lattices have been observed for a number of transition-metal perovskites and are fundamental in understanding the physical properties of many of these materials. For example, the formation of dynamic charge ordering fluctuations has recently been reported in superconducting $La_{1.85}Sr_{0.15}CuO_4$ [7] and $YBa_2Cu_3O_{y-x}$ [8] , while in $Pr_{0.7}Ca_{0,3}MnO_3$, a ferromagnetic metallic phase forms from the melting of a charged-ordered lattice when irradiated with x-rays [9]. Charge and orbital ordering in the manganate perovskites bring into focus the overall issue of the influence of electron-phonon coupling on the transport and magnetic properties of the materials. In this paper we report magnetic measurements on diperovskite $HoMn_2O_5$ single crystals. We found that this material is an insulator within the range of liquid helium to room temperatures. We also established that at temperatures lower than 18 K these crystals possess anti-ferromagnetic ordering.

II. SAMPLES AND EXPERIMENTAL METHOD

The polycrystalline orthorhombic $HoMn_2O_5$ was synthesized by a solid-state reaction of stoichiometric amounts of Ho_2O_3 and MnO_2 with purity of 99.99. Synthesis was performed for 48 h at 1050°C in oxygen atmosphere. Single crystals were grown by High Temperature Solution Growth Method using PbF_2 / PbO / B_2O_3. The flux consisting of $PbF_2 : PbO : B_2O_3 = 0.2 : 0.795 : 0.005$ was mixed with $HoMn_2O_5$ powder at a 10:1 ratio and annealed in a platinum crucible at 1200°C for 24 h in oxygen. After that the temperature was decreased down to 950°C at a rate of 0.5°C/h. The flux was decanted and crystals of typical size $1.5 \times 1 \times 1$ mm^3 were acquired. EDAX analysis of the obtained crystals showed a compact content of the $HoMn_2O_5$. XRD analysis at room temperatures revealed monoform compound orthorhombic structure from spatial group $P_{bam}(z = 4)$ with parameters of the elementary unit cell $a = 7.264(5)$ Å, $b = 8.476(3)$ Å, and $c = 5.670(8)$ Å. An elementary cell containing one molecule $HoMn_2O_5$ is shown in Fig.1. The samples were prepared in ISSP of BAS. We studied the electrical resistance of the obtained samples from liquid He to room temperatures by the means of the four-probe method and magnetization (mass) **M** in the direction of axis **c**. All measurements were carried out by the means of a Ballistic Magnetometer at the International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland. The magnetometer sensitivity was 0.1 emu, and the accuracy of temperature measurement was 0.1 K.

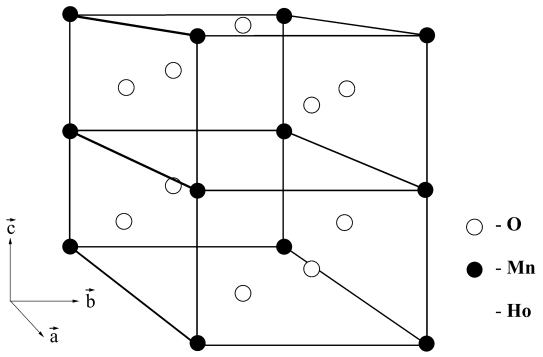

Fig. 1. Unit cell of one $HoMn_2O_5$.

III. RESULTS AND DISCUSSION

The studies on the electrical resistance of the samples revealed that they were insulators in the range between liquid helium and room temperature $-\rho = 1.3$ MOhm·cm. Fig. 2. depicts the correlation of the magnetic moment ($\mathbf{M}$) in the direction of the axis **c** of $HoMn_2O_5$ in the range 4.2–150 K and in the field $B = 1$ T. It can be observed that $\mathbf{M}$ increased with the decrease of temperature and at helium temperatures the curve tended to reach saturation. The magnetic moment was presented in Bohr's magnetron and correlated to one molecule $HoMn_2O_5$. $fu = 354.80$ g. Fig. 3. presents the magnetic moment in the direction as a function of the fields induction of up to 150 kOe at $T = 4.2$ K. The hysteresis shown on the figure is due to changes in the orientation of the magnetization vector $\mathbf{M}$ of the ferromagnetic domains in the direction of the external field $\mathbf{H}$. Due to the anisotropic $\mathbf{M}$, an internal effective field of magnetic anisotropy $\mathbf{H}_A$ was created, in the direction corresponding to the minimum energy. The magnetic hysteresis occurs due to the fact that in both directions $\mathbf{M}$ (in the direction of and against it) of the sample axis, definite conditions exist, limiting each other by a potential barrier proportionate to $\mathbf{H}_A$. The hysteresis during magnetization and demagnetisation of the ferromagnetics causes the so-called hysteresis losses. For one cycle, they can be presented by the integral $\oint \mathbf{H}\, d\mathbf{M}$, determining the area limited by the hysteresis curve. From the curve shown in Fig. 3. it can be seen that the samples are magnetically soft $M_r = 0.1\mu_B/fu$. The magnetic saturation at $T = 4.2$ K and the fields with induction of up to 145 kOe has the value of $M_s = 5.5\mu_B/fu$. The experimental data were treated in accordance with the Curie and Weiss theory, which states that the magnetic susceptibility $\chi = C'/(T - \Delta)$, where the constant C' corresponds to the Curie temperature in ferromagnetics or Neel's temperature, and Δ is the constant of the substance. Δ may have positive (ferromagnetic) conditions and negative (antiferromagnetic) conditions. For convenience, fig. 4 shows the correlation $1/\chi = f(T)$. From the slope of the straight line $C' = \cot\alpha$ can be determined, while is determined as the point of crossing of the straight line with the axis T. By means of such correlations it was established that $HoMn_2O_5$ samples were ferromagnetics at 18–191.5 K, while at temperatures lower than 18 K they were antiferromagnetics. For assessing the properties of such materials a spin charge and orbital-ordering studies are necessary. We have started to study the nature of the charge carriers by probing the electron asymmetry. The $HoMn_2O_5$ lattice is orthorhombic at room temperatures. It is composed of two $MnO_{2.5}$ layers, separated by a HoMn layer. Oxygen atoms are situated at the peaks of 2 octahedrons, which come in contact with their tops. At the point of contact of the two octahedrons Ho replaces the oxygen atoms. The manganese atoms of the HoMn layer are of 4^+ valency, while the Mn from the peaks of the octahedrons are from 3^+ valency. This causes asymmetry of the valency bonds deformation of the lattice. As a result, instead of tetrahedrical structure, an orthorhombic lattice is formed. Ho has an ionic radius that should, basing on tolerance factor considerations, allow a distorted perovskite structure. Our results indicate that Ho is indeed incorporated into the lattice. However, our experiments show that the extremely small Mn ions have thus resulted in an orthorhombic structure. This orthorhombic structure exhibits antiferroelectric behaviour, instead of the ferromagnetic state at low temperature.

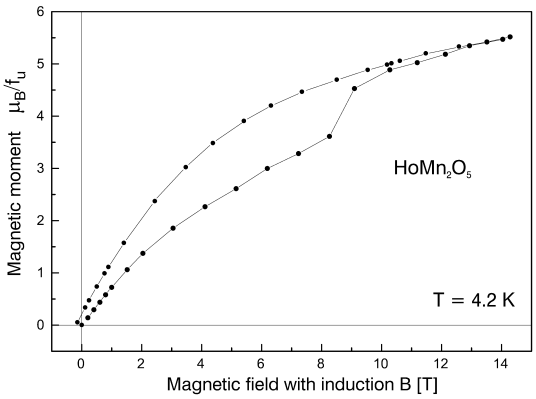

Fig. 2. The magnetic moment $\mathbf{M}$ in μ_B/fu units as a function of temperatute from 4.2 to 150 K in the field $B = 1$ T in the direction of the axis **c**.

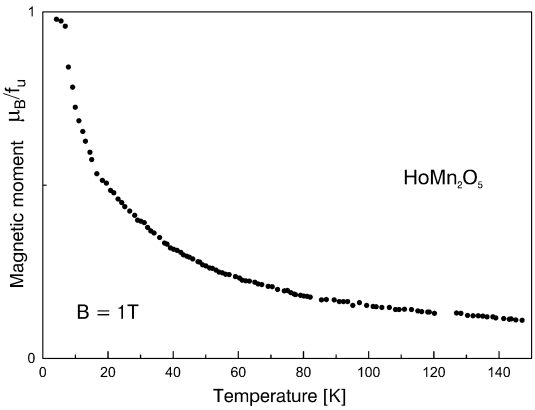

Fig. 3. Hysteresis correlation of the magnetic moment $\mathbf{M}$, μ_B/fu at $T = 4.2$ K and the fields with induction of up to 150 kOe.

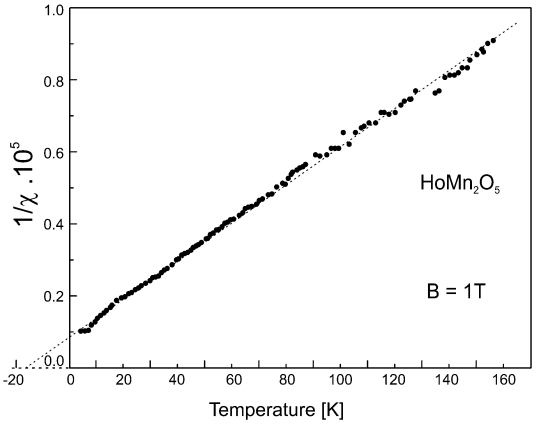

Fig. 4. The reciprocal value of the magnetic susceptibility $1/\chi$ as a function of temperature in the field $B = 1$ T. Negative values acquired with the crossing of the straight line $1/\chi$ with the temperature axis correspond to the antiferromagnetic condition of $HoMn_2O_5$.

IV. CONCLUSIONS

A. Charge and orbital ordering in the $HoMn_2O_5$ bring into focus the overall issue of the influence of electron–phonon coupling on the transport and magnetic properties of this material. The catastrophically weak conductivity of $HoMn_2O_5$ was due to the big width of the forbidden zone: the gap of this crystal. Charge-lattice fluctuations (electron-phonon coupling), which arise from the dynamic happing mechanisms such as polarons, are now generally accepted to play manganite perovskites [10]. The strong electron–phonon coupling associated with the charge ordering transition in $La_{0.5}Ca_{0.5}MnO_3$ has recently been described in terms of a charge density wave [11]. These measurements show that a BCS-like gap $2\Delta(T)$ fully opens at low temperatures and follows the hysteretic ferromagnetic–antiferromagnetic transition. B. In the analysis of single-crystals, the magnetic measurement data shows that the structure of $HoMn_2O_5$ is characterized by a partial charge localization. As described by Goodenough [12], the ordering of Mnd_{3z2-r2} orbitals in $La_{0.5}Ca_{0.5}MnO_3$ gives rise to staggered ferromagnetic interactions between filled Mn^{3+} and $Mn^{4+}d$ orbitals and antiferromagnetic interactions between the empty Mn^{3+} and Mn^{4+} orbitals. Under 18 K the crystal's structure from orthorhombic becomes tetragonal (space group $14/mmm$). Our analysis of single-crystals magnetic measurements shows that the charge and orbital ordering in $HoMn_2O_5$ are similar to that found in the perovskite manganates and predicted by Goodenough.

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СТРУКТУРА $HoMn_2O_5$, УТВОРЕНА ДВОШАРОВИМИ БЛОКАМИ ПЕРОВСКІТУ $[Mn_{0.5}O_{2.5}]$, ЩО РОЗДІЛЕНІ ШАРАМИ КАМ'ЯНОЇ СОЛІ HoMn

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Вивчено магнетні властивості шарових $HoMn_2O_5$ монокристалів в інтервалі температури 4.2–150 K та в магнетичних шарах з індукцією до 15 T. Установлено, що при кімнатній температурі кристали мають орторомбічну структуру та феромагнетні властивості. При температурах до 18 K кристали зазнають фазового переходу і стають антиферомагнетиками з тетрагональною структурою.