Photomagnetic effect in a single crystal of the bilayer manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

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The photomagnetic effect is investigated on a bilayered single crystal La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ manganite. The magnetization (M) enhancement induced by the laser (λ=532 nm) irradiation is observed in the whole studied temperature region. The increase of M is evaluated up to 10% and 15% by the light irradiation with laser power density 1.1 mW mm$^{-2}$ at 30 and 200 K, respectively. The three-dimensional (3D) ferromagnetic (FM) transition temperature $T_C$ is remarkably reduced under the light irradiation and the two-dimensional (2D) FM correlation temperature $T^*$ within the Mn-O bilayer is almost not affected by the light irradiation. The observed photomagnetic effect can be explained based on the photoinduced charge-transfer (CT) from O-2p ($p_z$) to Mn$^{4+}$-3d $e_g(d_{3z^2-r^2})$ orbital state.

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I. INTRODUCTION

Since the colossal magnetoresistance (CMR) effect was discovered in bilayer manganites La$_{2-x}$Sr$_x$Mn$_2$O$_7$ [belong to the $n=2$ member of the Ruddlesden-Popper series (La,Sr)$_{n+1}$Mn$_n$O$_{3n+1}$] by Moritomo et al.,$^1$ the study of layered perovskite manganites has attracted considerable attention because they display a rich variety of properties depending strongly on the doping level $x$. As is well known, the effective dimensionality of a system plays an important role on its physics properties. One of the most distinct features of layered perovskite manganites is its anisotropic characters in charge transport and magnetic properties because of the reduction of its effective dimensionality. In addition, the reduction of the dimensionality makes the ground state behavior of the system subject to the influence of external stimuli.

Recently, photomagnetic effects, defined as a response of magnetic properties of materials to optical stimuli (light irradiation), because of their possible potential applications in novel magneto-optical devices, have been extensively investigated in various magnetic materials,$^{2-9}$ e.g., a Prussian blue analog,$^2$ an organic-based magnet,$^3$ spin crossover complexes,$^4$ diluted magnetic semiconductor heterostructures,$^5$ spinel ferrite films,$^6$ orthorhombic perovskite colossal magnetoresistance (CMR) manganite films,$^7,8$ and hexagonal manganite single crystals.$^9$

Compared with the cubic doped perovskite manganites, the bilayer structure manganites should reveal a more delicate balance between ferromagnetic (FM) double exchange (DE) and antiferromagnetic (AFM) superexchange interaction because of its reduced dimensionality. Therefore, the ground state behavior of the bilayer manganites may display more sensitive properties to external stimuli. The photomagnetic effect is well known for materials mentioned above; however, it has not yet been observed for layered perovskite CMR manganites so far.

In this paper, we report the investigation as to the photomagnetic effect of a bilayer manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal. An obvious photoinduced increase of the magnetization and a dramatic decrease of $T_C$ are observed by the light irradiation. The results are suggested to originate from the photoinduced charge-transfer (CT) from O-2p ($p_z$) to Mn$^{4+}$-3d $e_g(d_{3z^2-r^2})$ orbital state.

II. EXPERIMENT

A single crystal of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ was melt grown in a floating-zone optical image furnace and in flowing 20% O$_2$ (balance Ar).$^{10}$ The crystal used here was cleaved from the resulting polycrystalline boules. The dc magnetization of the crystal was measured by means of a commercial superconducting quantum interference device (SQUID) magnetometer ($2 \leq T \leq 400$ K, $0 \leq H \leq 5$ T) in the temperature range of 5–390 K. For the light irradiation experiment, the light from a Nd-YAG laser was guided into the SQUID magnetometer through an optical fiber. The sample used in the experiment is a thin circle slice with the diameter of about 0.9 mm and the thickness of ~0.1 mm. The crystal surface was mechanically polished to a mirror surface. The resistance of the crystal was measured by the standard four-probe method in the SQUID system with both current and magnetic field directions perpendicular to the Mn-O bilayer from 5 to 390 K.

III. RESULTS AND DISCUSSION

The temperature dependence of the dc magnetization of the La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal measured under the zero-
field-cooled (ZFC) and field-cooled (FC) modes at an applied field of 0.01 T parallel \((M_{ab})\) and perpendicular \((M_c)\) to the Mn-O bilayer is shown in Fig. 1. It can be seen that \(M_{ab} > M_c\): the effect of the demagnetizing field due to the shape of the sample may play a main role on the anisotropy of the magnetization. A sharp transition is observed in both \(M_{ab}\) and \(M_c\) at \(T_s = 104\) K (defined as the peak temperature of \(dM/dT\) vs. \(T\) curve), signifying the three-dimensional (3D) FM ordering. Furthermore, there is a slight difference between FC and ZFC magnetizations at the low temperature region below about 50 K in both \(M_{ab}\) and \(M_c\) curves, which is usually ascribed to the appearance of the spin glass (SG) state induced by the competing interaction between FM double exchange (DE) and AFM superexchange interactions.\(^{11}\) Except for the transition at \(T_s\), Fig. 1 exhibits that there still exists another transition at \(T' = 275\) K (also defined as the peak temperature of \(dM/dT\) vs. \(T\) curve). \(T'\) is attributed to the appearance of two dimensional (2D) short-range FM correlation.\(^{12–14}\) In the inset of Fig. 1 we present the temperature dependence of out-of-plane resistivity \(\rho_c\) at zero and 4 T magnetic fields. As typically seen in other studies, \(\rho_c\) drops sharply by more than two orders of magnitude and a larger MR ratio is obtained under the applied magnetic field near \(T_s\).

The temperature dependences of FC magnetization of the La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal measured at \(\mu_0H = 0.01\) T under the condition of free-irradiation and laser irradiation with laser power densities \(P = 0.2, 0.6, \) and \(1.1\) mW mm\(^{-2}\) in real time are shown in Fig. 2. For \(M(T)\) measurements under the laser irradiation, the sample is irradiated at 300 K at a fixed laser power density and cooled at \(\mu_0H = 0.01\) T to low temperatures, then data are collected in the process of warming. The direction of the light beam and the magnetic field is perpendicular to the Mn-O bilayer. Additionally, in order to avoid the effect of the sample heating during the process of the light irradiation on the measuring results, the “settle” measuring mode is used, i.e., the magnetic moment begins to be measured after the temperature becomes stable for 60 s at each settled temperature point. Compared with \(M\) for the free-irradiation, \(M\) of the sample under the light irradiation is obviously increased, and \(M\) increases monotonously with \(P\) in the whole studied temperature range, as shown in Fig. 2. The variation of \(M\), defined as \(\Delta M = [M(P) - M(0)]/M(0)\), where \(M(0)\) and \(M(P)\) are the magnetization values corresponding to the free-irradiation and the light irradiation with \(P = 1.1\) mW mm\(^{-2}\), is estimated to be about 10% and 15% at \(T = 30\) and 200 K, respectively. Although \(M\) is increased due to the light irradiation, Fig. 2 exhibits that the Curie temperature \(T_c\) is remarkably reduced under the light irradiation, which can be clearly observed from the magnified plot of \(dM/dT\) vs. \(T\) as shown in the upper right inset of Fig. 2. The figure displays that the peak shifts to low temperatures with increasing \(P\). Compared with the \(T_c\) of the free-irradiation sample, \(T_c\) under the light irradiation with \(P = 1.1\) mW mm\(^{-2}\) is reduced about 9 K. The photoinduced relative variation of \(T_s\) is estimated to reach \(dT_c/dP = 8.2 K/(mW mm^2)\). Although both \(M\) and \(T_c\) are remarkably changed by the light irradiation, the 2D FM correlation temperature \(T'\) is almost not influenced by the light irradiation compared with the large variation of 3D \(T_c\) under the laser irradiation. The similar photomagnetic effect is also observed under the ZFC measuring mode (not shown here) and when the light is switched off after light irradiation at 10 K for 1 h as shown in the lower-right inset of Fig. 2.

To further test the photomagnetic effect of the La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal in the low temperature 3D FM region below \(T_c\), the 2D FM correlation region of \(T_c < T < T'\), and the critical region in the vicinity of \(T_c\), the magnetization of the sample under the light irradiation is measured at three fixed temperatures of 30, 200, and 100 K, respectively. First, the sample is field cooled to the settled temperature value, 30 K, at \(\mu_0H = 0.01\) T, and then magnetization is measured under the condition of free-irradiation. Second, the sample is irradiated by the laser with \(P = 1.1\) mW mm\(^{-2}\) at the same temperature point. The magnetization is measured after the temperature becomes stable at 30 K for 2 min. The obvious magnetization enhancement under the light irradiation...
The variation of magnetization under the light irradiation for the La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal at 30 K (a), 200 K (b), and 100 K (c). The laser power densities \(P_1\), \(P_2\), and \(P_3\) are 0.2, 0.6, and 1.1 mW mm\(^{-2}\), respectively.

As to the origin of the photomagnetic effect observed in orthorhombic perovskite CMR manganites, it is suggested to originate from the charge transfer (CT) from O\(_{2p}\) to Mn\(3d\) \(e_g\) orbit caused by the light irradiation,\(^{7,8}\) because CT between O-2p and Mn-3d orbits can be usually induced by light irradiation.\(^{16}\) As we know, the oxidation numbers of transition metal ions within a magnetic material can be modified due to CT caused by the light irradiation, which results in the magnetization variation because of the variation of the spin quantum number \(S\) of transition metal ions. For the origin of the photomagnetic effect observed in our studied layered manganite La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal, it is also reasonable to suggest that the photomagnetic effect may also be closely related to the CT from O-2p to Mn-3d \(e_g\) orbit caused by the light irradiation, because the result of temperature of optical conductivity spectra \(\sigma(\omega)\) indicates that the light irradiation with photon energy of above 3 eV and below 3 eV can cause the CT-type transition from O-2p to Mn \(3d\) \(t_{2g}\)-like (down spin) states and the intraband and interband CT-type transitions relevant to O-2p and Mn \(3d\) \(e_g\)-like state.\(^{17}\) For our experiment, the light source used is the laser with the photon energy of 2.33 eV (\(\lambda = 532\) nm), which can cause CT excitation from O-2p to Mn \(3d\) \(e_g\) orbit. But we suggest that the detailed CT process may be different from the 3D perovskite manganite due to the quasi-2D character of the La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) single crystal. For the crystal structure of La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\), the Mn-O bilayer alternates with the perovskite structure separated by the insulating rock-salt layer along the c-axis direction, which are misaligned with respect to each other. The similar projected plot along [010] as drawn by Argyriou et al.\(^{18}\) is shown in Fig. 4. As we know, for La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) there exists three kinds of FM exchange interactions, i.e., the FM exchange interaction \((J_1)\) in the Mn-O plane within the bilayer (called intraplanar exchange interaction), which originates from the overlap of oxygen \(p_s\) or \(p_y\) orbit with the \((d_{3z^2-r^2})\) orbit of Mn \(e_g\) electron; the FM exchange interaction \((J_2)\) between the Mn-O planes within the bilayer (called intrabilayer exchange interaction), which is caused by the overlap of oxygen \(p_x\) or \(p_y\) with the \((d_{3z^2-r^2})\) orbit of Mn \(e_g\) electron; and the FM exchange interaction \((J_3)\) between the Mn-O bilayers, which is due to the transport of \(e_g\) electron between the Mn-O bilayers when the sample lies in the metallic state. Based on the fact that no FM long-range order is observed for 2D single Mn-O layer La\(_{2-x}\)Sr\(_x\)MnO\(_4\) manganites,\(^{19}\) we suggest that the intra-bilayer exchange interaction \(J_2\) should play a crucial role in the formation of 3D FM long-range order of La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) manganites. There-
Therefore, both the magnetization increase and the $T_c$ decrease can be explained based on the photoinduced CT from O(2) $2p(p_z)$ to Mn$^{4+}$-3d $e_g (d_{3z^2-r^2})$ orbit. This kind of CT increases the proportion of the Mn$^{3+}$ ion which results in the increased magnetization of the crystal.

As to the reason of $T_c$ drop induced by the light irradiation, it is suggested to stem from the breaking of the optimal proportion between Mn$^{3+}$ and Mn$^{4+}$ ions in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ crystal caused by the CT. In addition, the CT from O$_{2p}$ to Mn 3d $e_g$ orbit by the laser irradiation increases the concentration of Mn$^{3+}$ Jahn-Teller (JT) ions and enhances the JT distortion, which weakens the exchange interactions $J_2$ and $J_3$ leading to the decrease of $T_c$. In addition, because the intraplanar FM interaction $J_1$, which is suggested to dominate the 2D FM ordering within the Mn-O plane, is much stronger than the intrabilayer FM interaction $J_2$ (Refs. 14 and 20) and the FM interaction between the bilayers $J_3$ is almost not influenced by the light irradiation, and this may be the possible reason that no obvious variation of $T^*$ is observed under the light irradiation.

**IV. CONCLUSION**

In summary, we have studied the photomagnetic effect on the bilayered manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal. The enhanced M induced by the light irradiation with the laser ($\lambda=532$ nm) is observed in the whole studied temperature region. The 3D FM transition temperature $T_c$ is obviously decreased under the light irradiation and the 2D FM correlation temperature $T^*$ within the Mn-O bilayer is almost not affected by the light irradiation. The observed photomagnetic effect is suggested to originate from the photoinduced CT from O-2p($p_z$) to Mn$^{4+}$-3d $e_g (d_{3z^2-r^2})$ orbital state.

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