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Magnetism of insulator Sr_2IrO_4 with strong spin–orbit coupling

Min Ge [a], Shun Tan [a,*], Yuanjie Huang [a], Lei Zhang [b], Wei Tong [b], Li Pi [a,b], Yuheng Zhang [a,b]

[a] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China
[b] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China

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ABSTRACT

The magnetic properties of polycrystalline sample Sr_2IrO_4 have been investigated by the magnetization, electron magnetic resonance (EMR), the infrared (IR) and Raman spectra measurements. Our experimental results indicate that the magnetism is determined by the effective total angular moment $J_{eff}=1/2$ instead of the spin with $S=1/2$. The temperature dependence of macromagnetic moment, resonance field of EMR line, A_{2u} mode of IR and A_{1g} mode of Raman spectra exhibit interesting behavior at about 40 K. Due to the Dzyaloshinskii–Moriya interaction, the magnetic order is canted, and the ferromagnetic component decreases with decreasing temperature. These complex magnetic behaviors in the system are attributed to the change of Ir–O–Ir bond angle with cooling, while the variation of bond angle is observed through the IR and Raman spectra.

1. Introduction

The 5d-electron based iridates have attracted considerable attention due to the interaction between strong spin–orbit coupling and other correlation interactions such as electron correlation and electron–phonon interaction [1,2]. Since 5d-electron orbitals are more extended and delocalized than 3d and 4d-electron orbitals, the bandwidth W (Coulomb interaction U on-site) should be much larger (smaller) than those of 3d and 4d orbitals, which leads to the weakness of electron correlation effects according to the simple band theory. Therefore, the 5d-based transition metal oxides were considered to be more metallic and less magnetic than the 3d-electron based oxides. However, many iridates are observed to show magnetic insulating behaviors recently, such as $Sr_3Ir_2O_7$ [1] and $J_{eff}=1/2$ Mott insulator Sr_2IrO_4 [2–34]. The energy of spin–orbit coupling in 5d-electron transition metal oxides is about 0.3–0.4 eV [11,35], which is comparable to the Coulomb interaction U on-site. So, the competition between the spin–orbit coupling with Coulomb and other energies will drive a variety of novel physical phenomena which have not been observed in other materials.

The layered perovskite Sr_2IrO_4 has a K_2NiF_4-type structure belonging to space group $I4_1/acd$. The IrO_6 octahedra rotate around the c-axis about 11° in the unit cell, which corresponds to a distorted in-plane Ir1–O_2–Ir1 bond angle. The distorted bond angle plays a key role in determining the electronic structure [16,19,24]. It is demonstrated that Sr_2IrO_4 is a weak ferromagnetic insulator driven by strong spin–orbit coupling [6]. In addition, it performs a giant magnetoelectric effect near 100 K [16]. More important, the theoretical calculation predict that it has possibility to be a high temperature superconductor if doped [20,24,26, 30,31]. The Mott insulating gap between upper and lower Hubbard bands in the $J_{eff}=1/2$ bands is induced by the Coulomb repulsion U (about 0.5 eV for Sr_2IrO_4) [7]. Therefore, exotic magnetic coupling representing the complex spin–orbital states are anticipated in this spin–orbit dominated compound [20].

In this work, we investigate the polycrystalline sample Sr_2IrO_4 by the X-ray diffractometion, electron magnetic resonance (EMR), infrared (IR) and Raman spectroscopy, and measurements of macroscopic magnetism. Our experimental results confirm that the magnetism of Sr_2IrO_4 is determined by the effective total angular moment $J_{eff}=1/2$ rather than the spin of $S=1/2$. We also find that 40 K seems to be an especial turning point, where M measured under magnetic field lower than 0.002 T decreases with cooling below 40 K. Moreover, A_{2u} mode of IR and A_{1g} mode of Raman spectra shift with temperature decreasing and the blue shift are also small below 40 K. It is suggested that the ferromagnetic component decreases with temperature decreasing because the size of the canted moment depends on the bond angle between Ir and O.

2. Experiment

The polycrystalline sample Sr_2IrO_4 was prepared by standard solid-state synthesis method. The starting materials, powders of $SrCO_3$ (purity 99.9%) and IrO_2 (purity 99.9%)) were mixed uniformly according to the stoichiometric ratio. The mixed powder was heated slowly to 1103 K in an Al_2O_3 crucible. After holding for

* Corresponding author. Tel.: +86 139 5698 0528.
E-mail addresses: gemin@ustc.edu.cn (M. Ge), tans@ustc.edu.cn (S. Tan).

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24 h, the sample was cooled down to room temperature. Then the powder was ground and pressed into round-shaped pellets and heat treated at 1273 K for another 2 days.

Structure and phase purity were checked by the Rigaku-TTR3 X-ray diffractometer using high-intensity graphite monochromatized Cu Kα radiation. The powder X-ray diffraction proves that the sample is a single phase with tetragonal cell belonging to the space group $I4_1/acd$. The temperature dependence of magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer. The EMR spectrum was recorded using electron spin resonance (ESR) spectrometry in the X-band at the microwave frequency of 9.4 GHz. The IR transmission spectra were obtained (Bruker Vertex 80v) by using powder sample with CsI serving as a carrier. The Raman scattering measurements were performed using a Horiba Jobin Yvon T64000 Micro-Raman instrument with a Kr^+-Ar^+ mixed gas laser ($\lambda = 514.5$ nm) as an excitation source in a backscattering geometry. The special Janis ST-500 Microscopy cryostat can provide a temperature range from 5 K to 300 K using liquid helium as its cooling source.

3. Results and discussion

The X-ray diffraction patterns, as shown in Fig. 1, demonstrate that the cell of Sr_2IrO_4, at selected temperatures from 15 K to 300 K is in the $I4_1/acd$ space group without impurities. For Sr_2IrO_4, different a and c axes have been reported previously by different groups, ranging from 5.4846 to 5.4994 Å for a and 25.766 to 25.804 Å for c [2,4–6,9,12]. Herein, it is calculated the lattice constants to be 5.4950 Å and 25.800 Å for a and c at 300 K. One can see that the shift of peaks is very tiny from 300 K to 15 K, which is induced by the thermal expansion obviously. Therefore, there is no structure transition in Sr_2IrO_4 and its structure is almost unchanged with decreasing temperature.

Fig. 2 depicts the temperature dependence of magnetization $M(T)$ for Sr_2IrO_4 in the zero-field cooling (ZFC) and field cooling (FC) processes under fields of 0.001 T, 0.002 T, 0.2 T and 1 T. There is a sharp magnetic transition at approximately 240 K, which has been reported for both polycrystalline [2–5,8] and single crystal samples [6,16,24]. Above 240 K, the susceptibility follows a modified Curie–Weiss law, as shown in the inset of Fig. 2(a). The magnetic ground state of Sr_2IrO_4 is canted antiferromagnetic state, which produces a residual ferromagnetic component in the IrO_2 planes. The origin of canted antiferromagnetic state is the Dzyaloshinskii–Moriya (DM) interaction derived from the spin–orbit coupling with the rotation of IrO_6 octahedra [14,15]. The corresponding $M(T)$ curves measured in ZFC and FC processes show the conspicuous magnetic irreversibility. The behavior observed in our polycrystalline sample may be induced by the magnetocrystalline anisotropy or the layer-by-layer disorder of canted-FM moments. It is notable that the magnetic moment decreases slightly with temperature decreasing measured under the FC process with 0.001 T and 0.002 T below 40 K, as shown by arrows in Fig. 2(b), which demonstrates that the total ferromagnetic moment decreases with temperature decreasing. Conversely, the upturn of $M(T)$ under 1 T (shown in Fig. 2(a)) which is also observed in single crystal [16], means that, a magnetic field of 1 T is large enough to influence the canted antiferromagnetic state.

In order to ascertain the magnetic behavior at low temperature, the field dependence of magnetization for Sr_2IrO_4 are measured from 5 K to 40 K in the field range of $-7 \le H \le 7$ T, as shown in Fig. 3. As can be seen, a significant magnetic hysteresis exists, which is a typical characteristic of the ferromagnetism. As we know, in a conventional ferromagnet, the magnetic moment should strengthen and tend to be more saturated at lower temperature. It is strange that the magnetic moment remains unchanged when the temperature decreases from 40 K to 5 K. Moreover, the slope of $M(H)$ in high field region increases rather than decreases with the decrease of temperature, as shown in the inset of Fig. 3. These abnormal phenomena confirm that the magnetic order is canted in Sr_2IrO_4, and the ferromagnetic component varies with temperature.

To explore the canted magnetic order in Sr_2IrO_4 especially at low temperature, the micromagnetism in this system was further investigated by the EMR. Fig. 4 shows the differential

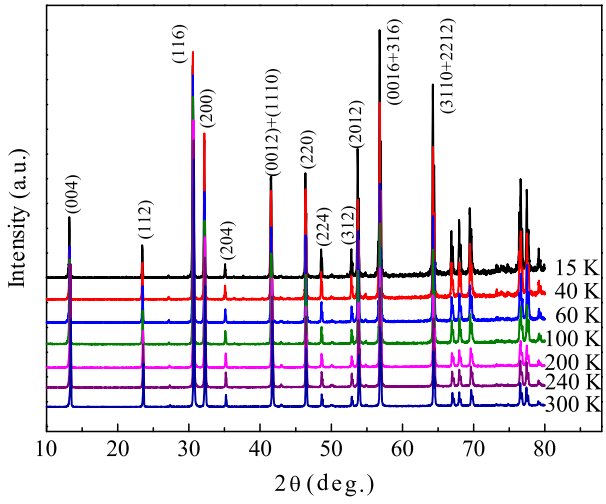

Fig. 1. (Color online.) X-ray diffraction patterns of the polycrystalline sample at selected temperatures from 15 K to 300 K.

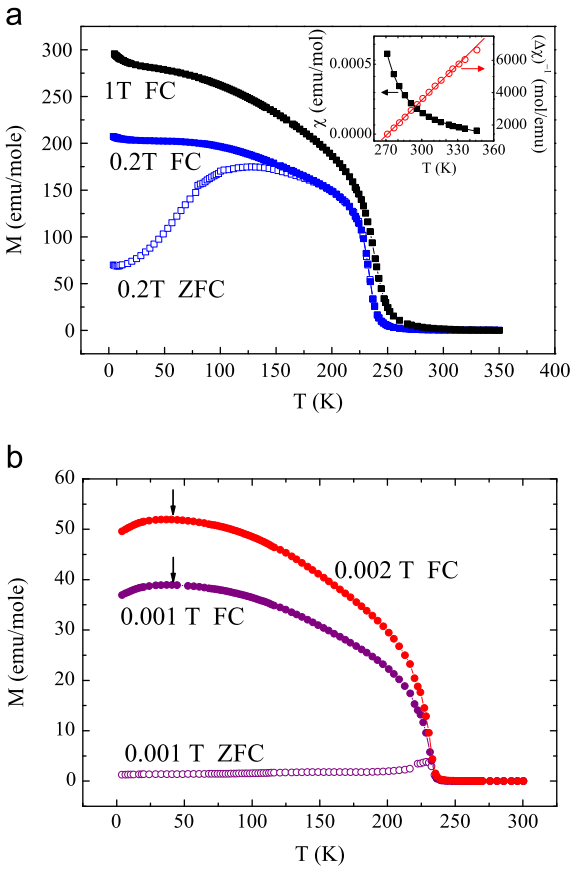

Fig. 2. (Color online.) Temperature dependence of the magnetization $M(T)$ measured under (a) 0.2 T and 1 T; (b) 0.001 T and 0.002 T. The inset of (a) shows $\chi(T)$ in the paramagnetic region, measured under 1 T along with a plot of $(\Delta\chi)^{-1}$ versus T where $\Delta\chi = \chi - \chi_0$.