ESRF	**Experiment title:** x-ray absorption magnetic circular and linear dichroism study of spin-orbit coupling and orbital occupation on single crystal Sr2IrO4	**Experiment number**: HC-704
Beamline: ID12	**Date of experiment**: from: 24/04/2013 to: 29/04/2013	**Date of report**: 19/05/2014
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Report:

The observed insulating nature in the layered perovskite Sr_2IrO_4 is very surprising [1]. The Coulomb energy U in the 5d shell is generally considered to be very small as compared with 5d band width W, and, hence, a metallic behaviour is expected. Considerable efforts have been paid recently to explain the insulating nature of Ir oxides [2-8]. A rather unconventional explanation is that the large spin orbit coupling (SOC) splits the 5d t_{2g} band into several narrow sub-bands, the lowest of which is the $\tilde{J}$ =1/2 with a band width smaller than U so that the Hubbard insulating state can be formed. This model is based on the idea that the strong crystal field on the Ir^{4+} ion with $5d^5$ configuration leads to a low spin t_{2g}^5 configuration (S=1/2). This t_{2g} shell transforms effectively as a p shell, giving a value of 1 for its orbital quantum number l (one hole in the shell). The modified third Hund's rule says that l is coupled with S anti-parallel arriving at $\tilde{J}$ =1-1/2=1/2 [2-8]. However, The Ir-$L_{2,3}$ XMCD experiments revealed the experimental ratio between orbital and spin moment m_l/m_s =1.05 for Sr2IrO4 [9] and 1.4 for BaIrO4 [10], which are much smaller than 2 predicted for a pure ionic J_{eff}=1/2 ground state. They therefore proposed a strong mixed J_{eff} =1/2, and 3/2 scenario, challenging the popular model for the iridates. Another important quantum number is <**L**·**S**> which is expected to be 1 for pure J_{eff} =1/2 according to <**L**·**S**> = $-1/2[J_{eff}(J_{eff}+1)- l(l+1)-S(S+1)]$, while the experimental value is about 2 for Sr_2IrO_4 [9] and $BaIrO_3$ [10] based on branching ratio (BR) = $I(L_3)/I(L_2)$, where $I(L_{2,3})$ is the integrated XAS intensity. Moreover, there is considerable confusion in the community about the alignment of the orbital and spin contributions to the magnetic moment. Some think they should be *parallel*, but others think that it should be *anti-parallel* on the basis of the above arguments. A parallel L_z and S_z alignment was found from XMCD experiments [8,9].

Sr_2IrO_4 has a distorted tetragonal structure and an antiferromagnetically but weak canted ferromagnetic moment of 0.14 μ_B/Ir in ab-plane. The previous XMCD measurement on Sr_2IrO_4[9] for a powder sample and using only 0.8 Tesla magnetic field is far from sufficient to draw far reaching conclusions concerning the validity of the J_{eff}=1/2 scenario, although they have further ruled out the pure J_{eff}=1/2 ground state based on nonzero XMCD signal at the Ir-L_2 edge, which was however scaled by factor 333 in order to compare XAS intensity.

During the allocated beamtime at the ID12 beamline we have carried out x-ray magnetic circular dichroism (XMCD) experiments at the Ir-$L_{2,3}$ edge on single crystals of Sr_2IrO_4 at temperatures 6 K and 50 K in a high magnetic field of 17 T. To compare previous work by Haskel *et al*. [9], we have also measured spectra at 6 K in an applied field of 0.8 T. The spectra were measured in two different geometries, i.e. with the magnetic field (and the Poynting vector of the circularly polarized photons) parallel to **a** and **c** axes. We first look at the

XMCD spectra taken at 6 K under 0.8 T presented as blue line in Fig. 1. We can see no XMCD signal for H//**c** at both the Ir-L_3 and the Ir-L_2 edges and a clear XMCD signal at the Ir-L_3 edge for H//ab. The observed anisotropy of the XMCD signal is in agreement with magnetization data [1]. Note that XMCD signal reported in Fig.1 is scaled only by factor 25, while the L_3 and L_2 XMCD data were scaled by factor 100 and 333, respectively, in ref. 9.

The main XMCD signal at Ir-L_3 edge lies at 3 eV below the main peak in XAS spectrum in agreement with ref. 9. This energy shift can be understood considering that only the *t2g* orbitals contribute to the XMCD signal, while both t_{2g} and e_g orbitals contribute to the XAS spectrum with the XAS maximum corresponding to the signal from the unoccupied e_g levels. Therefore, this energy position difference corresponds to the effective crystal field splitting 10Dq [10] between the t_{2g} and e_g orbitals. This is much larger than 1.8 eV used in previous theoretical calculation [9]. There is a very weak XMCD signal at the Ir-L_2 edge in H//ab (bottom right), which increases with increasing magnetic field. Since its existence was assigned to an indication of deviation from a J_{eff} =1/2 ground state, therefore we have to carefully look this feature. We find that (1) the energy position of the weak XMCD signal lies above, but not below the main XAS peak at the Ir-L_2 edge, therefore is not the t_{2g} related feature. (2) it is very delocalized and extends more than 10 eV above the main XAS peak. (3) such a high lying XMCD signal can be also observed in the Ir-L_3 edge as indicated by an arrow (bottom left). Our above observations demonstrate that this spectral feature might be originated from 6s related states hybridized with Ir 5d states.

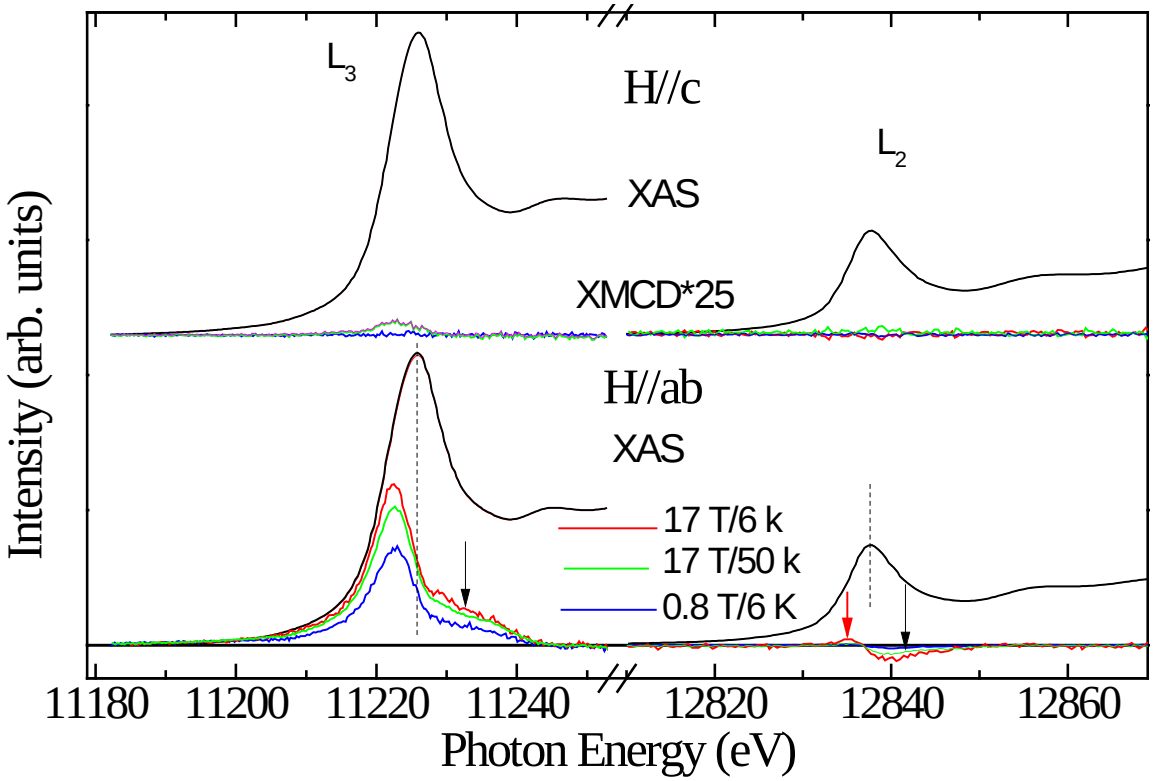

FIG.1 The black lines are Ir-$L_{2,3}$ XAS spectra of Sr_2IrO_4 taken with magnetic field parallel to c (top) and parallel to ab-plane (bottom). Blue, green and red lines are XMCD data taken at T=6 K/H = 0.8 T, T = 50 K/H = 17 T and T = 6 K/H = 17 T, respectively.

Very weak XMCD signal at the Ir-L_2 edge as has the same origin as those found in the previous resonant experiments, such as the resonant inelastic x-ray scattering (RIXS) and the resonant resonant x-ray diffraction (RXD) [3-5]. Although this behavior was proposed to the arrangement of the t_{2g} orbital and spin of t_{2g} electrons [3-5], our simulations suggest that the SOC of Ir^{4+} verwhelms the t_{2g} splitting and strongly suppresses the t_{2g}-related peak at the L_2 edge. This strong difference between the L_3 and L_2 edges for a LS d^5 was already known in the $4d^5$ transition metal compounds [11]: one t_{2g} hole contributes its spectral weight at the L_3 edge, but not the L_2 edge if SOC interaction is larger than t_{2g} splitting.

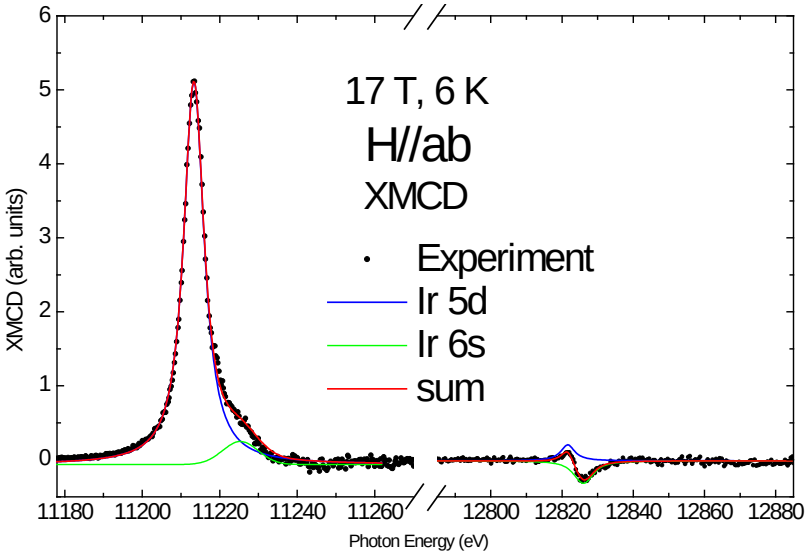

Fig. 2. Simulation of XMCD signal contributed by Ir 5d (blue) and 6s (green) states.

Very recently theory indicates that RIXS is zero irrespective of the tetragonal distortion [12], therefore RIXS is insensitive to the degree of deviation from J_{eff} =1/2.

XMCD measured along easy magnetic direction in ab-plane under 17 T is enhanced by about factor 3 with respect to that taken at 0.8 T for powder sample [9]. This has improved the accuracy by using sum rules.
If we remove 6s contribution to XMCD signal, we have $m_l/m_s(1+7m_T/m_s)=2(\Delta L_3+\Delta L_2)/3(\Delta L_3-2\Delta L_2)= 0.73$, where $\Delta L_3(\Delta L_2)$ is integrated XMCD, m_T is the magnetic dipole moment. This is 15% more than that found previously [9]. Our IC calculations present the ratio of $(1+7m_T/m_s) = 1.98$, then, *we get* m_l/m_s =1.54, which is smaller than 2 expected for pure 1.05 J_{eff} =1/2, but much larger than 1.05 found previously [9]. Very recent nonresonant magnetic x-ray diffraction observed a 40% enhancement of m_l/m_s *[13]*.

We have observed strong polarization, magnetic field and temperature dependent XMCD signal at the Ir-$L_{2,3}$ edge of single crystal Sr_2IrO_4. The weak XMCD at the L_2 edge is mainly originated from more extended 6 s states. Although *orbital moment* and spin moment is antparallel, L_z and S_z have a parallel alignment. The large 5d SOC favors formation of a pure J_{eff}=1/2 for the t_{2g}^5 states, however, the weak tetragonal distortion and intra-atomic multiplet interaction as well as exchange interaction lead to a strong mixture of t_{2g} and e_g states and a deviation from pure J_{eff}=1/2.

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