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XMCD measurements under pressure confirm ferromagnetism in $YbCu_2Si_2$ but find none in $YbRh_2Si_2$

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Abstract.
$YbCu_2Si_2$ and $YbRh_2Si_2$ have a similar phase diagram above 8GPa. While $YbCu_2Si_2$ is a well-known valence fluctuating compound that orders probably ferromagnetically above P_c=8GPa, in $YbRh_2Si_2$ the nature of the magnetic order at high pressure remains unclear. However, the fact that ferromagnetic (FM) fluctuations are found at low pressure leads to a robust speculation that the high pressure order could be FM. In this work, we have investigated the magnetic order induced by pressure in both compounds, by means of XMCD spectroscopy. Our measurements have confirmed the ferromagnetism in $YbCu_2Si_2$ through a clear saturation in the magnetization for pressures above P_c. On the other hand, the XMCD signal for $YbRh_2Si_2$ remains weak even at 25 GPa, pointing out a clear difference between the high pressure ordered phase of these compounds, and suggesting that FM order is unlikely if not completely excluded.

1. Introduction

In the last three decades, heavy fermion (HF) compounds have been extensively used to investigate quantum critical phenomenon, as they can be relatively easily tuned through a quantum phase transition[1]. These intermetallic compounds are situated between the classical rare-earth ones, with well localized f electrons, and the intermediate-valence ones, for which a strong mixing of f and conduction electrons is observed. In the HF systems, the f shell occupation number weakly deviates from integer value, leading to an ambiguous character of the f electrons (itinerant versus localized) at low temperatures, with strong low energy magnetic and/or valence fluctuations.

At least for Ce and Yb based HF systems, the Doniach picture can be used as starting point to understand their behavior at low temperature. In the Kondo lattice model, the magnetic moments, coming from the $4f$ electrons, form a regular sublattice that can present nonmagnetic or magnetically ordered ground states due to the competition between on-site Kondo and

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intersite RKKY interactions. In this scenario the competition is governed by a single parameter, the effective exchange constant J between local moments and conduction electrons, which is usually tuned by chemical or physical pressures. Such a change in hybridization has opposite effects in Ce and in Yb based compounds, since pressure acts driving Ce away from its magnetic trivalent configuration ($4f^1$), while favoring it ($4f^{13}$) in Yb case.

Although the Ce and Yb Kondo lattices can be considered electron/hole equivalents, Yb compounds also offer a favorable opportunity for studying the role of the valence fluctuations in the quantum criticality, since applied pressure is expected to induce larger changes of the valence[2]. As an example, valence instability was directly observed in the tetragonal $YbCu_2Si_2$ compound under pressure by Resonant Inelastic X-ray Scattering measurements[3]. This is an ideal prototype Yb system, presenting a moderate $\gamma = 135 mJmol^{-1}K^{-2}$[4], that obeys Doniach's phase diagram. With pressure, the system evolves from a paramagnetic state to an ordered one[5, 6], reached at the critical pressure $P_c \approx 8GPa$. The nature of the ordered phase was investigated by AC susceptibility[7] and magnetization[8, 9] measurements, that strongly suggest that the induced magnetic order is ferromagnetic (FM). The phase transition close to P_c may be of first order, as pointed out by Mössbauer measurements[10, 11], that have found a spectrum with two well-separated non-magnetic and magnetic components (Yb magnetic moment $\approx 1.25\mu_B$), although transport measurements close to the critical pressure find a behavior very similar to the predicted effects of a second order quantum phase transition[6].

In contrast to an abundant number of antiferromagnetic (AF) Kondo lattice systems, for which the AF quantum critical point (QCP) has been intensively investigated, until recently there was no good equivalent example for a direct transition from a FM to a paramagnetic ground state. Another interesting compound that may help to find a reason for the scarcity of systems with FM QCPs is the intensively studied system $YbRh_2Si_2$. Its phase diagram at low pressures is quite complex, however at high pressures it is rather similar to $YbCu_2Si_2$[12](see figure 1), showing also a clear anomaly in the specific heat above 8GPa at a temperature which reaches about 4K at 12 GPa[13]. In this compound, both FM and AFM fluctuations were found to coexist[14]. However, above 5GPa, FM coupling seems to play the dominant role[13]. Hence, investigations of ferromagnetism in these compound, using a direct probe are highly desirable.

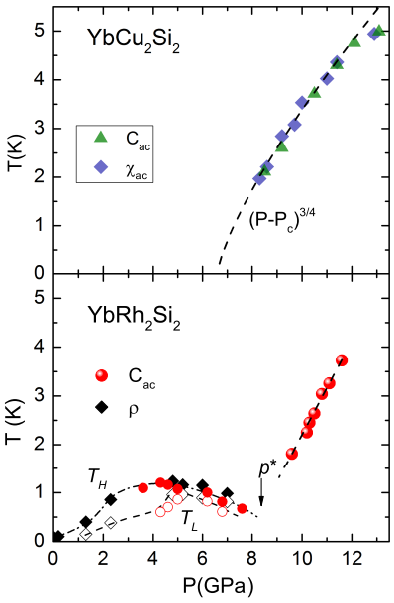

Figure 1. Adaptation from the literature [3, 13] of the phase diagrams of $YbRh_2Si_2$ and $YbCu_2Si_2$ compounds, showing a clear similarity between the shape of magnetic phases above 8GPa.

The objective of this work is to investigate the high pressure phase in both compounds by means of X-ray Magnetic Circular Dichroism (XMCD) spectroscopy in order to shine some light over the nature of the ordered state in $YbRh_2Si_2$. XMCD spectroscopy is a very powerful element specific and orbital-selective magnetometry technique[15]. Its great advantage lies in the possibility to determine both the spin and the orbital magnetic moments in amplitude and direction of the absorbing atom. The combination of this technique with recent advances in high pressure technology has offered unique possibilities in understanding the physics of magnetic materials under extreme conditions. XMCD spectroscopy under high pressure has become now a well established technique, and contrary to macroscopic measurements, it does not suffer from spurious magnetic traces coming either from the sample environment, such as the cell and gasket, or magnetic impurities in the sample itself.

2. Experimental details

The measured X-ray absorption spectra of atoms in magnetic solids depend on sample orientation, X-ray polarization and external magnetic field. The dichroism effect is given by the difference of the X-ray absorption intensities, measured for photons with positive and negative angular momentum aligned along the fixed magnetization direction of the sample. It can be measured either by changing the photon circular polarization or by switching the magnetization direction. Our approach is to apply XMCD spectroscopy under pressure to probe the magnetism of the Yb via the L_3 absorption edge, instead of M_4 one, which is usually selected when investigating rare-earth based compounds. The strong hybridization between f and d electrons (Yb^{3+} - $2p^6 4f^{13} 5d^1$) creates an equivalence between measuring the Yb L_3 edge and the Yb M_4 one. The last would be preferable but it is not possible to perform XMCD measurements under pressure in that edge because of the diamond absorption. For rare-earth elements, the L_3 absorption edge consists of two separated contributions, mainly due to electric dipole transitions (E1: $2p \rightarrow 5d$) but also due to electric quadrupole transitions (E2: $2p \rightarrow 4f$). In the case of Yb, these two contributions are well separated in energy (7eV), as shown in Fig 2 a, although it remains very difficult to quantitatively estimate directly the $4f$ magnetic moments without a reference sample. Further, even after separating the two contributions, the application of the sum rules to the E1 contributions yields a wrong sign of the $5d$ magnetic moments due to a spin-dependence of the transitions matrix[16]. Nevertheless, the intensity of the XMCD signal at the E2 transitions is directly proportional to the magnetization of the $4f$ magnetic moments.

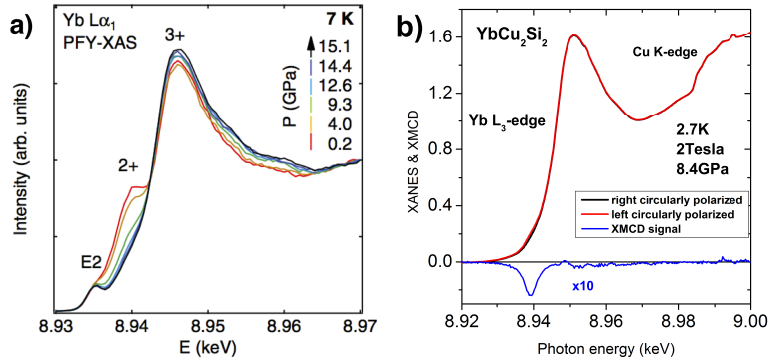

Figure 2. a) X-ray absorption spectra (XAS) recorded in partial fluorescence yield mode (PFY) at 7K for $YbCu_2Si_2$, showing the quadrupolar peak E2[17]. b) XANES (X-ray absorption near edge structure) for right and left circularly polarized beams and the XMCD signal, recorded at 2.7K and 8.4GPa with field along c-axis.

By using XMCD measurements we expected to be able to see a clear difference between the signals of two phases of the $YbCu_2Si_2$ compound, below and above P_c, if the ordered state is indeed FM. And by comparing those two signals with the one obtained for $YbRh_2Si_2$, we expected to obtain a relative value for the magnetization of that compound, also above and below P_c.

Both samples were prepared by In-flux method described in the literature[6]. In the case of $YbCu_2Si_2$, the high value of the residual resistivity ratio (RRR >200) of the samples used indicates a very high crystal purity, implying no (or only extremely limited) indium substitution on the Si or Cu sites[3]. For the $YbRh_2Si_2$ case, the measured RRR of the crystals [13] was about 300 and the residual resistivity ρ_0 <1$\mu\Omega$cm.

Two synchrotron beam lines were used on this work. At the European Synchrotron Research Facility (ESRF) ID 12 beamline[18], a single crystal $YbCu_2Si_2$ sample was installed into a membrane driven variable pressure cell loaded with He gas as the pressure medium[19]. The cell was mounted on a ^{4}He constant flow cryostat cooling the sample down to a constant temperature of 2.7K. The pressure was changed *in situ* and measured by the fluorescence of a ruby chip placed inside the pressure chamber. A 6T superconducting split-coil was used to magnetize the sample. The external magnetic field was aligned parallel with the $YbCu_2Si_2$ sample's easy

magnetization axis, i.e. c-axis. The as-measured element specific magnetization curve was recorded by monitoring the Yb L_3-edge XMCD signal at E2 energy as a function of applied field at 2.7K. For each magnetic field point, the helicity of the x-ray beam was reversed twice in opposite order to ensure artefact free measurements.

On the second experiment, performed at the French National Synchrotron Facility (SOLEIL) ODE beam line[20], powder samples were installed in membrane driven variable diamond pressure cells filled with silicon oil as a pressure medium. A helium circulation cryostat was used to achieve a temperature of 4.1K. This time, the magnetic field direction was reversed, while the beam helicity remained constant.

3. Results

Considering that the intensity of the XMCD signal at the E2 transitions is proportional to the magnetization of the $4f$ magnetic moments on rare-earth elements, we have measured the field dependence of the XMCD signal in order to probe directly the magnetic state of the Yb atoms on $YbCu_2Si_2$. The obtained XMCD spectra were determined as the direct difference between the normalized x-ray absorption spectrum for Yb L_3 edge recorded with right circularly polarized beam and the spectrum recorded with left circularly polarized beam. The order of magnitude of the XMCD signal normalized to the edge-jump of unity was nearly 2% . Figure 2 b shows an example of absorption spectrum obtained and the XMCD signal for a field of 2T. The element specific magnetization curves up to 2T, applied along c-axis, for different pressures at 2.7K are presented in figure 3. An almost linear dependence on magnetic field can be seen at 5.7GPa, while signs of saturation start at 7.6GPa. A strong increase in signal amplitude can also be seen above P_c. At 10.7GPa there is a clear change of slope with a start of saturation at about 0.2T, typical behavior of a FM. We did not measure $YbRh_2Si_2$ in similar conditions as the single crystals grow in thin platelets making it almost impossible to measure with the field in the easy (a,b) plane. Instead both compounds were measured in powder form.

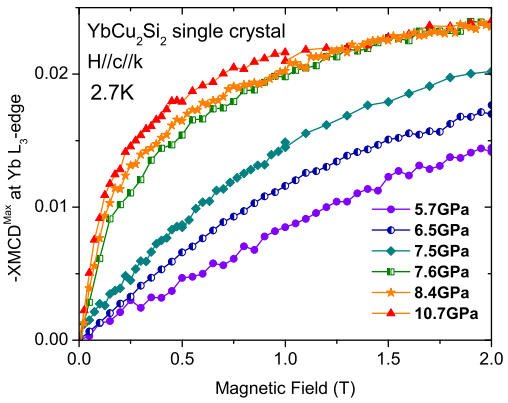

Figure 3. The element specific magnetization, measured at 2.7K and different pressures, for $YbCu_2Si_2$. The saturation tendency at high pressures confirms the FM nature of the ordered phase above P_c.

Spectra obtained for both compounds on the SOLEIL ODE beam line, by dispersive X-ray absorption spectroscopy (DXAS), can be seen in figure 4, where the XMCD signal is also displayed. At ambient pressure the intensity of the signals for both compounds is almost the same. However, when the pressure is increased, the signal for $YbCu_2Si_2$ starts to increase slowly and at 5.7GPa it is already much stronger then the one for a pure paramagnet signal (figure 5). Above this pressure the signal increases drastically pointing out the proximity of a ferromagnetic phase. As for the $YbRh_2Si_2$ compound, the XMCD signal remains weak and roughly constant for the whole pressure range. At the highest pressure achieved its signal is one order of magnitude smaller than the $YbCu_2Si_2$ one.

4. Discussion and conclusion

We know that the XMCD amplitude is directly proportional to the magnetic moment at the saturation condition. In $YbRh_2Si_2$, above 8.5GPa, the valence of the Yb ion is near three, and valence fluctuations are completely suppressed [13]. On the other hand, for the $YbCu_2Si_2$ compound the valence of the Yb varies continuously without reaching the fully trivalent state at least until 22GPa [3]. In principle, if the high pressure phase for both compounds was FM, measurements at the same conditions would give XMCD signals that behave similarly. The simple and most likely explanation is that the high pressure order in $YbRh_2Si_2$ is AF. The sensitivity of the measurement would not permit to observe decrease of susceptibility when going from the paramagnetic (PM) to AF state.

We must however take into account two points: first, we are not completely sure to be in the ordered state in $YbRh_2Si_2$. The SOLEIL measurements were made at 4.1K, slightly above the highest ordering temperature measured for $YbRh_2Si_2$ (3.6K at 12GPa), although the slope of the phase boundary strongly suggests that, at pressures achieved in this experiment (up to 22GPa), the ordering temperature would easily exceed 4.1K. Futhermore, both the a.c. susceptibility and magnetization measurements on $YbCu_2Si_2$ show a strong increase several Kelvins above the ordering temperature, which addictionally should be enhanced with field for a FM. So, a FM phase with a similar ordered moment as $YbCu_2Si_2$ (more than $1\mu_B$) can almost certainly be ruled out for $YbRh_2Si_2$.

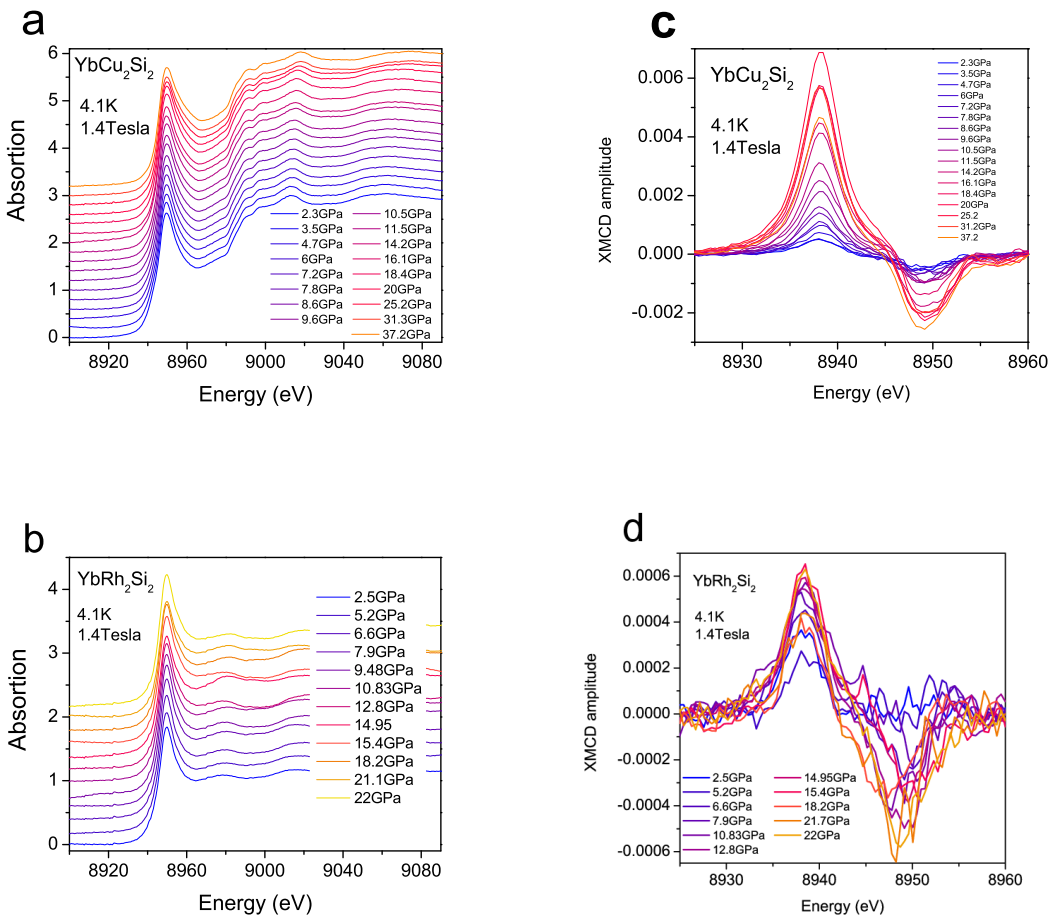

Figure 4. DXAS spectra (a, b) and XMCD signal (c, d) for $YbCu_2Si_2$ and $YbRh_2Si_2$, respectively, measured in powdered samples at 4.1K and 1.4T.

The second point to consider is that, for Co doped $YbRh_2Si_2$, FM order has been found but with a small moment ($0.1\mu_B$) and, surprisingly, along the hard (c) axis of the pure compound.[21] As our experiment was performed on a powder sample, FM order should be detected whatever the direction of the moments. However, we estimate by comparison with $YbCu_2Si_2$ and the moment detected from Mössbauer results ($1.25\mu_B$) in the system, that $0.1\mu_B$ is about the limit of detection in our experiment. So, a FM phase with a weak ordered moment at high pressure cannot be completely ruled out.

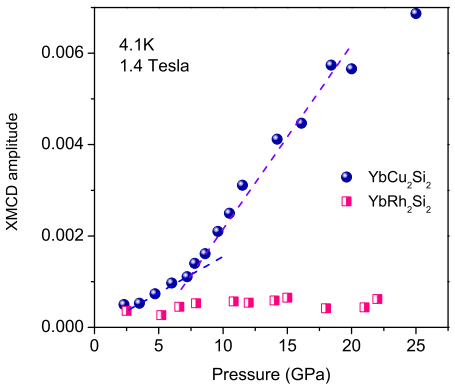

Figure 5. XMCD amplitude as a function of pressure.

Anyway these results point out a clear difference between the high pressure ordered phase of these compounds, and showing that FM order at high pressure in $YbRh_2Si_2$ is finally unlikely if not excluded. XMCD measurements at lower temperatures and higher magnetic fields must be performed to exclude, without doubts, the possibility of ferromagnetic order on the $YbRh_2Si_2$ compound above 8.5GPa.

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