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► **To cite this version:**

L. Joly, J.-P. Kappler, P. Ohresser, Ph. Saintavit, Y. Henry, et al.. Kondo screening of the spin and orbital magnetic moments of Fe impurities in Cu. *Physical Review B*, 2017, 95 (4), pp.041108. 10.1103/PhysRevB.95.041108 . hal-03989093

HAL Id: hal-03989093

<https://cnrs.hal.science/hal-03989093>

Submitted on 14 Feb 2023

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Kondo screening of the spin and orbital magnetic moments of Fe impurities in Cu.

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(Dated: March 14, 2016)

We demonstrate by analysing a model dilute Kondo alloy that x-ray magnetic circular dichroism (XMCD) is able to evidence the Kondo regime. The temperature evolution of the d spin and orbital magnetic moments of Fe impurities in highly diluted Cu:Fe alloys is measured. XMCD is also a unique technique which enables the direct and separate measurement of the spin and orbital moments of a Kondo impurity.

The Kondo effect [1] is a paradigm of the many body interactions that originates from the hybridization of strongly correlated electron orbitals with a continuum of free-electron like metal states. It is well understood for a single spin $S = 1/2$ from the Anderson impurity model (AIM) [2] or from the related s - d Kondo model [3, 4]. *Via* spin flip-excitations at 0 K, the impurity and the continuum host states form a coherent many-body singlet state, where the impurity spin state is completely screened by the host continuum states [3, 5]. With increasing temperature, the system exhibits a crossover [6] at the so-called Kondo temperature T_K , from a low temperature local Fermi liquid state [3, 5] to a high temperature magnetic regime characterized by a free spin behavior corrected by logarithmic temperature terms. It was noted early that a correct description of experiments should take into account orbital degrees of freedom, crystal field effects, Hund's rule coupling, localized Coulomb and exchange interactions [7], but all these points remain very challenging. For example, recent theoretical studies of the Au:Fe system [8, 9] propose different low energy effective models (n -channel model [10], orbital dependent Kondo effect [11]) to interpret magnetotransport and decoherence experiments. Studies combining density functional theory (DFT) and quantum Monte-Carlo [9, 12], or non-crossing approximation reveal the importance of multi-orbital effects and the difficulty to determine a reliable value of the Kondo temperature [13]. For the Cu:Fe dilute alloy, an archetype of dilute Kondo system [3, 14, 15], the n -channel model with $n = 4$ and $S = 2$ fits the Mössbauer magnetization and specific heat data [16]. This implies that the Fe impurity is in a Fe^{2+} spin and orbital singlet state. These assumptions, and in particular the lifting of the orbital degeneracy on a energy scale larger than the Kondo temperature are however not fundamentally justified.

From an experimental viewpoint, classical magnetom-

etry techniques typically measure the macroscopic susceptibility and do not provide information at the level of the impurity itself. On another hand, scanning tunneling microscopy has provided useful information about the spatial and structural dependence of the Kondo effect [17–19], but details on the magnetic configuration itself remains inaccessible. X-ray magnetic circular dichroism (XMCD) has the sensitivity to measure low concentrations, typical of such systems. It has also the unique capability to separate in a direct way spin and orbital moments with chemical selectivity. XMCD may therefore become an interesting tool to investigate orbital effects in Kondo systems, as for example the possibility of different screenings for spin and orbital moments.

Here, we investigate the crossover from the free paramagnetic limit to the Kondo screened state using XMCD in the Cu:Fe dilute system. We provide the first separate measurement of the spin and orbital magnetic moments in an extended temperature range. We show that the spin magnetic moment is strongly reduced below the Kondo temperature, whereas the orbital moment remains constant in the explored temperature range. The Cu:Fe system is well suited for such studies, since its Kondo temperature (≈ 20 K) provides an experimentally sizeable temperature range below T_K as well as above in the paramagnetic phase, where the magnetic signal rapidly decreases with temperature.

The fabrication of dilute alloys for Kondo effect measurements is critical and two main difficulties have to be overcome. The first one is the formation of magnetically coupled Fe pairs: too large concentrations lead to non negligible pair formation. Since the Kondo temperature of pairs (T_K^{pair}) is much lower than T_K for isolated impurities, at temperatures between T_K^{pair} and T_K , the paramagnetic pair signal will dominate [20, 21]. Therefore, the impurity concentration should be kept as low as possible. The second one is related to sample oxidation. Copper is

indeed not a good barrier against oxygen penetration and Fe oxidizes near the sample surface. Contrary to conventional techniques, in x-ray absorption spectroscopy, the oxide signal can be identified and subtracted, so that more accurate results can be obtained. Two series of polycrystalline dilute Cu:Fe alloys were prepared. A first series of bulk alloys was obtained by a melting preparation technique [20]. A second series was prepared in form of thin films by magnetron sputtering in ultra-high vacuum conditions (base pressure in the low 10^{-9} mbar range). This method was used successfully in earlier Kondo effect experiments [22]. Films of 200 to 350 nm were deposited on transparent SiC membranes (200 μm thick). They were grown at room temperature by co-deposition from a pure Cu target and a mixed Cu:Fe one containing 1% at. Fe. The evaporation rates (≈ 1 nm/s) were adjusted to obtain the desired composition. After fabrication, the samples were kept at ≈ 100 K to avoid atomic diffusion which may lead to clustering of Fe impurities (*i.e.*, yielding a paramagnetic pair magnetization) [20]. The electrical resistivity of the samples was determined by a conventional 4-point resistance technique. X-ray absorption Spectroscopy (XAS) experiments were performed at the SIM beamline at the Swiss Light Source on the French cryo-magnet end-station. The absorption spectra were recorded at the $L_{2,3}$ edges of Fe in a ± 6.5 T magnetic field in the 2 K to 150 K temperature range. The field was parallel to the incident photon beam, normal to the sample surface. XMCD spectra were obtained by switching both the x-ray helicity and the direction of the magnetic field. Doing so removes any possible spurious asymmetries and yields reliable dichroic signals. The bulk samples obtained by melting were analyzed by total electron yield (TEY) and the thin film samples by TEY and transmission. Because of the very small Fe concentration and weak magnetic signal, XMCD was only measured with the largest available field. At each temperature, about 80 energy scans, representing 6 hours of acquisition time, were averaged to obtain the XMCD signal.

Two samples were measured: a 2500 ppm sample obtained by melting, and a thin film sample with 500 ppm. The first one yields larger Fe signal, but with important pair interaction, whereas the second one provides negligible pair interaction. The Fe concentrations were estimated by measuring the edge jump intensity at the Fe L_3 edge. They agree within $\approx 10\%$ with the nominal concentrations. The measured Kondo minima of the resistivity are respectively 21 K (500 ppm) and 40 K (2500 ppm), in excellent agreement with earlier measurements [23]. In the following we will focus on the 500 ppm thin film sample. The results for the 2500 ppm are discussed in the Supplemental Material.

A significant contribution of oxidized Fe is visible in the absorption spectra in both TEY and transmission modes. The TEY spectra are characteristic of the sur-

face and they are of pure oxide character. Note that the oxide spectra are not comparable to those of conventional bulk Fe oxide. They rather reveal a mixture of various environments of Fe in a small crystal field as expected for cubo-octahedral or tetrahedral symmetries [24, 25]. The transmission spectra are characteristic of the whole sample, including a surface contribution (Figs. 1a and b). They contain contributions from both unoxidized and oxidized Fe atoms (Fig. 1c). The oxide contribution to the transmitted XMCD signal can be removed by subtracting the TEY signal measured on the same sample, after proper normalization. Such procedure to separate different contributions has already been applied successfully to other systems [26, 27].

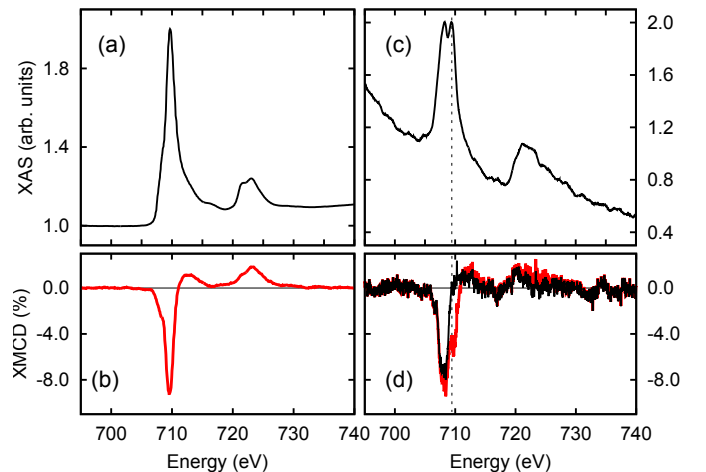


FIG. 1. (Color online) XAS and XMCD signals for a 500 ppm Cu:Fe sample on SiC membrane. a) XAS in TEY mode; b) XMCD in TEY mode; c) XAS in transmission; d) XMCD in transmission before (red) and after (black) subtraction of the oxide contribution. The vertical dashed line identifies the position of the oxide feature. The spectra are recorded in a ± 6.5 T field and at 10 K.

Applying the sum rules [28, 29] (see Supplemental Material for a discussion on their validity) on the oxide-corrected Fe XMCD signal allows extracting the spin and orbital magnetic moments as a function of temperature. More precisely, the projections of the moments per atom along the photon beam direction (parallel to the magnetic field) are actually determined. The XMCD signal intrinsically contains a contribution from $2p \rightarrow 4s$ transitions, which can however be neglected since their absorption cross section is very small compared to the $2p \rightarrow 3d$ transitions (≈ 100 times smaller) [25]. Since the samples are polycrystalline and likely cubic, the magnetic dipolar term (T_z) to the spin sum rule can also be safely neglected, as usual for intermetallic compounds [30].

Let us first examine the m_l/m_s ratio (Fig. 2). It has the advantage to be independent of the number of d holes, which is generally obtained from DFT calculations [31]. One notices two regimes: a constant ratio

in the low temperature range, which coincides with the low-temperature Kondo regime observed in the resistivity (Fig. 2 inset), and an increase above ≈ 40 K. There is currently no available theory able to calculate the temperature dependence of the m_l/m_s ratio for a Kondo system. Only Ligand Field Multiplet (LFM) calculations allow estimating this ratio, but they do not take into account Kondo correlations and are not well appropriate for describing materials with strong band character like metallic systems. Nevertheless, they give an idea of what is expected for a non-Kondo system. For a free ion in spherical symmetry, the m_l/m_s ratio is constant, provided temperature does not mix states with different total orbital momenta. However, when a crystal field is present m_l/m_s becomes temperature dependent. Some sets of LFM parameters fairly reproduce the observed behavior (see Supplemental Material). Therefore, in the absence of a reliable calculation including Kondo correlation, one cannot draw conclusions from the m_l/m_s ratio. In particular, one cannot conclude on different Kondo screenings for spin and orbital moments. We will therefore have to analyze separately a m_l and m_s .

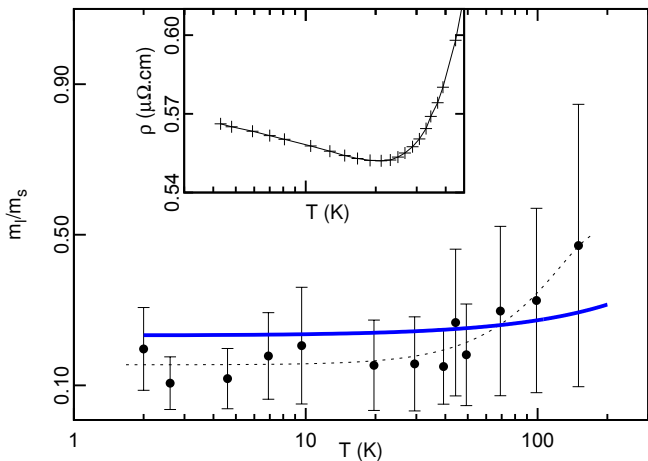


FIG. 2. (color online) Orbital to spin moment ratio m_l/m_s as a function of temperature for the 500 ppm sample in a 6.5 T field, as determined from the sum rules. The dotted line is a guide to the eye. The full (blue) curve is a LFM calculation for an Fe ion in a $3d^7$ configuration in a dodecahedral symmetry with $10Dq = 0.25$ eV and a reduction of the atomic Slater integral parameters of $\kappa = 0.8$ (see Supplemental Material). Inset: low temperature resistivity as a function of T for the same sample on a semi-logarithmic scale. Note the characteristic $\ln(T)$ Kondo behavior of the resistivity at low temperature.

To do so, the XMCD signal must be normalized to the white line integral, which is proportional to the number of d -holes [31]. The white line integral reveals to be temperature independent, indicating no charge evolution with temperature. We can therefore take a calculated number of d holes from DFT calculations to estimate ab-

solute values of m_s and m_l . These calculations show that the number of d holes for an Fe impurity embedded in a Cu matrix and for bulk Fe are identical within $\approx 0.5\%$ (see Supplemental Material). Here, we take $N_d = 3.37$.

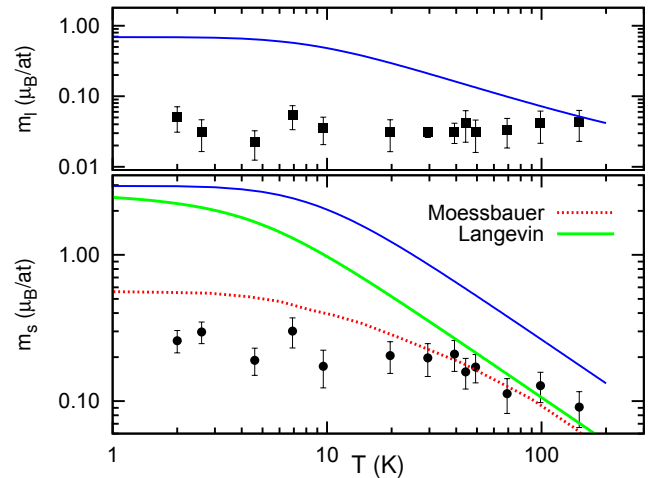


FIG. 3. (Color online) The lower and upper panels display respectively d -spin (disks) and orbital (squares) moments as determined from sum rules as a function of temperature for the 500 ppm sample in a 6.5 T field. The blue lines are respectively the spin (bottom panel) and orbital (top panel) moments given by a LFM calculation for an Fe ion in the same configuration as in Fig. 2. The paramagnetic Langevin function for a single atom magnetic moment of $m_s = 2.7 \mu_B$ in a 6.5 T field is plotted as a full green line ($m_s = 2.7 \mu_B$ is the value obtained by DFT calculations for Fe in Cu). Mössbauer data from Steiner *et al.* are represented as a dashed red line. These data were interpolated to 6.5 T for enabling comparison with the present experiment.

Figure 3 shows the variation with temperature of the spin and orbital d -magnetic moments per atom in a 6.5 T field as deduced from XMCD sum rules. First, one notices that the measured spin moment at low temperature is much smaller (≈ 10 times) than the value one would expect for a paramagnetic Fe atom. This very weak value is spectacularly different from what is observed *e.g.* for isolated atoms on surfaces, which show magnetic moments of several Bohr magnetons at these temperatures [32, 33], but it is indeed expected from Kondo screening. For comparison, a Langevin function [34] (green line) assuming a spin moment of $2.7 \mu_B$ per atom (as obtained by DFT for Fe in Cu) is plotted, together with the spin moment obtained by LFM calculations (blue line) for an Fe ion in a crystal-field. None of the models reproduce the experimental behavior of m_s (see Supplemental Material). Second, the spin moment exhibits a crossover from a nearly temperature independent regime, identified as the Kondo regime, to a free-atom behavior for $T \geq T_K$. Note that the 2500 ppm sample yields both similar temperature evolution and spin moment per isolated Fe atom. The analysis is however more complicated

since it requires removal of a paramagnetic Fe pair signal (see Supplemental Material).

The only earlier measurements of the local Fe impurity magnetization on this system were performed by Mössbauer spectroscopy [35]. These data are shown as a dashed red line in Fig. 3. Although the XMCD determined spin moments are smaller than those measured by Mössbauer spectroscopy, the two behaviors obtained by completely different local experimental techniques agree qualitatively.

The orbital moment is almost constant with temperature and is extremely weak. It is in good agreement with the value obtained with DFT, but not with LFM calculations who give much larger values, except if the Slater integrals are strongly reduced (see Supplemental Material). The intrinsically small orbital moment unfortunately does not allow to get significant information of the effect of Kondo correlations.

In summary, we show that XMCD is able to identify the signature of the Kondo effect in the temperature dependence of an impurity magnetic moment. The crossover from the Kondo regime to the free atom-like paramagnetic regime of an Fe impurity in dilute Cu:Fe alloys is measured. XMCD has the unique advantage of a direct measurement of both spin and orbital magnetic moments. It opens up the possibility to get better insight in multi-orbital and spin-orbit effects. XMCD should also become an interesting complement to scanning tunneling spectroscopy for *in situ* studies on Kondo systems like atoms and molecules on surfaces.

Acknowledgments We are grateful to B. Muller from IPCMS and the SIM beamline staff at Swiss Light Source for their help in setting up the installation. We would also like to thank N. Lorente, and J. Merino, T.O. Wehling for fruitful discussions. Financial support from CNRS PICS-program, contract N° 5275 is acknowledged, as well as computational time from the Institut du Développement et des Ressources en Informatique Scientifique (Project No. i2014092291)

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