Attempt to Probe the Ground State of $YbInNi_4$ by New Spectroscopic Techniques

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In order to understand complex correlations in matter it is necessary to model its ground state properties. Here, spectroscopy by neutrons and X-rays has become an ever more important tool. We employed these tools in combination with magnetometry in an effort to determine the nature of the ground state in $YbInNi_4$. $YbInNi_4$ was originally studied when the first order, temperature driven isostructural valence transition in $YbInCu_4$ was discovered [1] where (as in many rare earth Kondo and/or heavy-fermion compounds) the 4*f* electrons couple to the conduction electrons. It is therefore evident that any attempt to understand the first order valence transition in $YbInCu_4$ requires the knowledge of the wave functions of the 4*f* electrons involved, especially since a non-isotropic hybridization of individual crystal-field (CF) states might have to be considered [2,3]. The CF scheme of $YbInCu_4$ cannot be studied directly because of its low temperature intermediate valence state, so that $YbInNi_4$, which is trivalent over the entire temperature range, has been studied instead. Yet $YbInNi_4$ by itself is very intriguing. Several investigations have been carried out in the last two decades, but each investigation proposed a very different crystal field scheme [3–6]. We therefore set out to investigate the crystal-field scheme of $YbInNi_4$ with soft X-ray absorption spectroscopy (XAS), polarized neutron diffraction and inelastic neutron scattering. In an extensive study of transport and thermodynamic measurements on $YbInNi_4$ [7] ferromagnetism arising at 3 K was found. We extended the field and temperature dependent magnetization measurements down to 500 mK. While the precious low field data [7] are in agreement with our findings, the present data show the importance of antiferromagnetic exchange interactions and geometrical frustration.

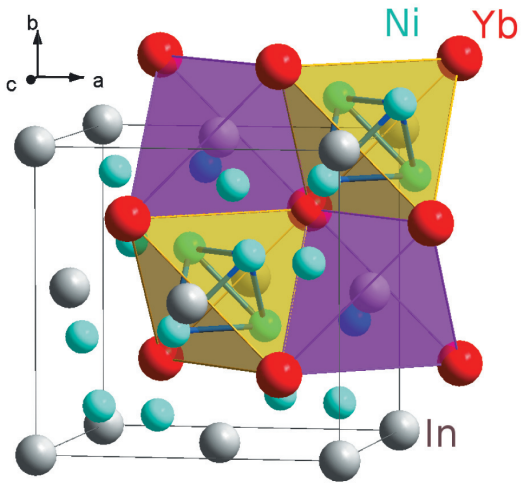

Fig. 1: Unit cell of $YbInNi_4$.

Magnetic Field induced Dichroism in X-ray absorption spectroscopy

The non-centrosymmetric cubic C15b ($AuBe_5$) structure of $YbInNi_4$ is shown in Figure 1. The Yb and In ions reside on distinct face-centered-cubic sublattices displaced by (1/4, 1/4, 1/4) along the unit cell diagonal and are surrounded by space-filling Ni tetrahedra. The tetrahedra formed by the magnetic Yb ions are alternately intercalated with the Ni tetrahedra (light yellow tetrahedra in Fig. 1) or filled with In ions (dark pink tetrahedra in Fig. 1). In this cubic structure the crystal field (CF) splits the 8-fold degenerate $J = 7/2$ Hund's rule ground state of Yb^{3+} into two doublets (Γ_6 and Γ_7) and one quartet (Γ_8).

The $M_{4,5}$ ($3d \rightarrow 4f$) XAS spectrum for the Yb^{3+} consists of one single line, no matter whether the ground state is Γ_6, Γ_7 or Γ_8: the final state has a full $4f^{14}$ shell, and the intensity is all concentrated in the $3d_{5/2}$ resonance (M_5 absorption edge), since transitions to the $3d_{3/2}$ state (M_4 absorption edge) are dipole forbidden in the limit that the CF splitting is negligible compared to the 4*f* spin-orbit splitting. None of these CF states show a polarization dependence for linearly polarized X-rays com-

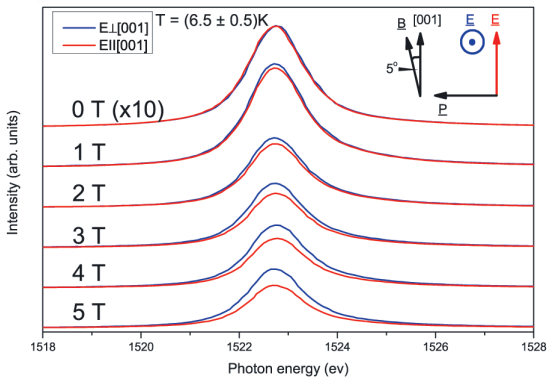

Fig. 2: Measured magnetic absorption at the M_5 edge for light polarized parallel (red) and perpendicular (blue) to the [001] direction for several field strengths. The top right sketches the experimental set-up: The magnetic field B is 5° off the 90° position to the Poynting vector P, i.e. 5° off the sample [001]. The incoming light is polarized parallel and perpendicular to [001].

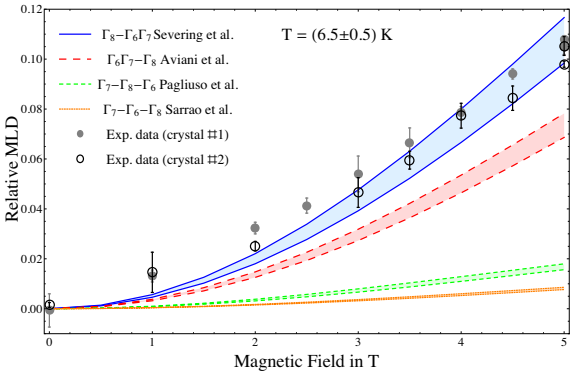

Fig. 3: Normalized MLD versus field. The full and empty circles correspond to measurements of two different $YbInNi_4$ crystals. The coloured trails are MLD simulations for the four CF scenarios for temperatures between 6 K and 7 K.

ing in with the electric field vector parallel or perpendicular to the [001] crystallographic axis, since all states are cubic.

The situation changes considerably when a magnetic field is applied, *e.g.* along the [001] or z-axis. Apart from inducing a Zeeman splitting, the Γ_8 state becomes split into the $\widetilde{\Gamma}_6$ and $\widetilde{\Gamma}_7$ states. The "~" indicates that and refers to irreducible representations of the tetragonal point group D_{2d}, which is a subgroup of the cubic point group T_d. While the 4*f* spatial distribution of the Γ_6 and Γ_7 states does not change, that of Γ_8 is transformed into quite different looking spatial distributions of the $\widetilde{\Gamma}_6$ and $\widetilde{\Gamma}_7$ states. It is important to note that the spatial distributions of $\widetilde{\Gamma}_6$ and $\widetilde{\Gamma}_7$ are not cubic. Consequently, there will be a linear polarization dependence for these two states. A polarization dependent XAS experiment in a magnetic field can therefore give a simple yes/no answer to the question, whether the ground state in a cubic material is a quartet or a doublet.

The experiment has been realized at the High-Field End Station on ID08 at the European Synchrotron Radiation Source (ESRF) in Grenoble. In our measurements [8] the magnetic field was about 5° off the 90° position in order to avoid the Lorentz force hindering the electrons to escape the sample. Two single crystals were cleaved in ultra-high vacuum and spectra have been obtained in different magnetic fields (see Fig. 2). By comparison of simulated and measured magnetic linear dichroism (MLD) signals it turns out that a Γ_8 quartet ground state is the most likely scenario for the CF in $YbInCu_4$.

Magnetic Form Factor Analysis

We have also measured the low temperature magnetic form factor, which probes directly the ground state wave function as Fourier transform of the spatial distribution of the 4*f* electron moment, i.e. it is directly sensitive to the anisotropy of the CF ground state. The magnetic scattering intensity in an elastic neutron scattering experiment is determined by the magnetic structure factor F_M

$$F_M = \frac{r_o}{2\mu_B} \left| \sum_n \boldsymbol{m}_n(\mathbf{Q}) \exp(i\mathbf{Q}\mathbf{R}_n) \exp(-W_n) \right| \qquad (1)$$

here **m(Q)** is the Fourier transform of the ionic magnetization density at the scattering vector **Q.** The index *n* denotes the summation over different atoms of the magnetic unit cell, $\exp(-W_n)$ is the Debye-Waller factor and R_n the position of the *n*-th atom, μ_B is the Bohr magneton, and $r_0 = \gamma\, e^2/mc^2 = -0.54 \cdot 10^{-12}$ cm with $\gamma = -1.92$ the gyromagnetic ratio of the neutron. A polarized neutron diffraction experiment was performed on an $YbInNi_4$ single crystal using the D3 diffractometer at the high flux reactor of the Institut Laue-Langevin in Grenoble [9]. The peak intensity of the Bragg reflections which is measured for neutrons polarized parallel and antiparallel to the applied magnetic field, leads to the so-called flipping ratio $R = I^+/I^-$. To deduce the magnetic contribution from *R*, a good knowledge of the nuclear structure factors F_N is necessary. This was achieved by an experiment on the same crystal on the 4-circle diffractometer D9 at ILL. For **m(Q)**||**H** the flipping ratio *R* can then be written:

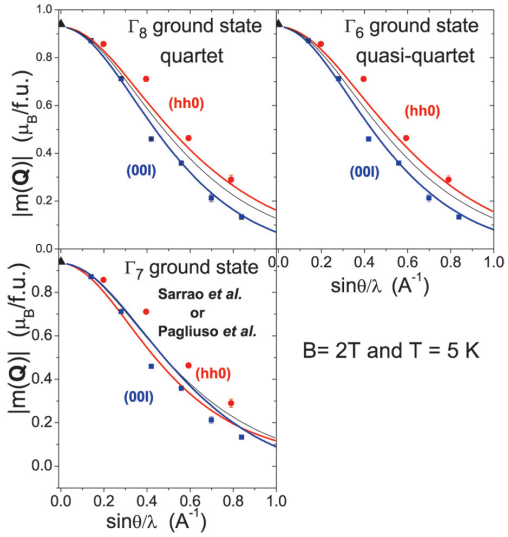

Fig. 4: Comparison of simulated ytterbium magnetic amplitudes |**m(Q)**| at $T = 5$ K for different ground states. The full symbols are the measured values for (00l) (blue squares) and (hh0) (red circles), the lines are simulations for the (00l) (blue) and (hh0) (red) directions for the different crystal-field propositions. The black line corresponds to the spherical form factor. The values for $\sin\theta\ \lambda^{-1} = 0$ (black triangles) come from magnetization.

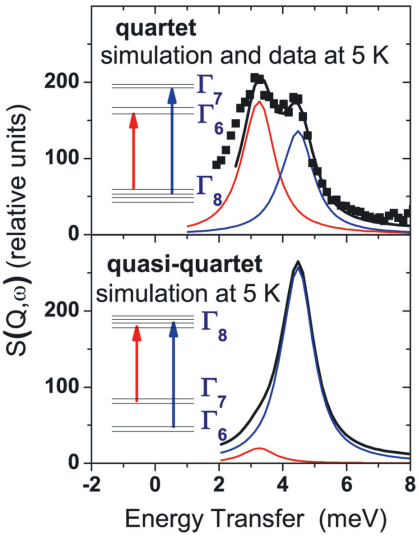

Fig. 5: Simulated inelastic scattering function at $T = 5$ K for a quartet (top) and quasi-quartet (bottom) ground state crystal-field model. The symbols indicate the experimental scattering function of $YbInNi_4$ for 12 meV incident energy and |Q| in between 0.35 Å^{-1} and 2.3 Å^{-1}.

$$R = \frac{F_N'^2 + F_N''^2 + 2\sin^2\alpha\, F_N' F_M + \sin^2\alpha\, F_M^2}{F_N'^2 + F_N''^2 - 2\sin^2\alpha\, F_N' F_M + \sin^2\alpha\, F_M^2} \qquad (2)$$

F_N' and F_N'' are the real and imaginary parts of the nuclear structure factor F_N and α is the angle between the magnetic moment **m(Q)** and the scattering vector **Q.** The F_M values deduced from the measured flipping ratios are directly related to the Fourier transform of the Yb^{3+} magnetization density **m(Q)** for the scattering vector **Q** (see eq.(1)). Figure 4 shows the obtained |**m(Q)**| values at 5 K and 20 K versus $\sin\theta\ \lambda^{-1}$ with $|\mathbf{Q}| = 4\pi\ \sin\theta\ \lambda^{-1}$. We have now simulated |**m(Q)**| for the different crystal-field scenarios. Our form factor measurements clearly rule out the possibility of Γ_7 as ground state. In contrast, the simulations for the Γ_6 ground state of the quasiquartet scenario and the for the Γ_8 quartet both give the correct anisotropy.

Neutron Spectroscopy

Inelastic neutron scattering experiments were done at the time-of-flight spectrometer MARI at the pulsed neutron source ISIS with an incident energy of 12 meV. The magnetic scattering intensity between 2.5 meV and 6 meV clearly consists of two lines (see Figure 5). Because of selection rules this new set of data can also only be described with a Γ_8 quartet ground state. A simulation of the scattering function for a quasi-quartet ground state excludes this possibility as an explanation for the inelastic neutron data of $YbInNi_4$ (Fig. 5): neither at 2 K nor at 5 K is the first excited doublet at 1 meV sufficiently populated to give rise to two almost equally strong excitations. This is demonstrated in Figure 5 where the result of a CF simulation with a quasi-quartet ground state is shown for 5 K.

Magnetic Order

In order to investigate the magnetic order at temperatures below 3 K some isothermal magnetization measurements in fields up to 5 T and temperatures down to 500 mK were performed using a vibrating sample magnetometer (VSM) in a physical property measurement system (PPMS) by Quantum Design and a SQUID magnetometer using a ^{3}He cryostat. Care was taken in an effort to minimize the remanent field of the superconducting magnet.

Figure 6 shows the isothermal magnetization data of $YbInNi_4$ at several temperatures between 2 K and 300 K and for fields up to 5 T along the crystallographic (100) direction. For all temperatures the

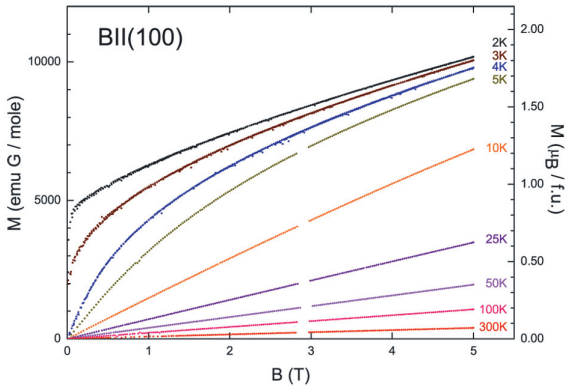

Fig. 6: VSM - Isothermal magnetization as a function of field at various temperatures.

magnetization still increases monotonically up to 5 T, i.e. it is far away from saturation. Below 4 K the onset of a magnetic transition becomes obvious and below 3 K the systems appears magnetically ordered. Field loops were measured for 0.5 K, 2 K, 3 K, and 4 K, i.e. just above and within the magnetically ordered state. Hysteresis was not observed within the accuracy of this experiment.

The assumption of a canted antiferromagnetic ordered state can explain the observations above. In the range of 5 to 10 mT the resulting ferromagnetic moment is aligned along the external field. It would also explain the small size of the ordered moment. A field of only 50 mT overcomes the antiferromagnetic exchange, so that a more paramagnetic response is observed for larger external fields. Hence we conclude that $YbInNi_4$ orders in a weak, possibly canted antiferromagnetic structure.

At first sight it seems surprising that a simple cubic structure leads to a non-trivial ordered state. A possible explanation might be in the crystallographic *fcc* (C15b) structure of $YbInNi_4$ where the magnetic Yb ions form two sub-networks of corner sharing tetrahedra (see Figure 1), so that simple next-nearest neighbor antiferromagnetic interactions will give rise to frustration. For the isostructural compounds $R InCu_4$, R = Gd, Dy, Ho, and Er strong signs of antiferromagnetic geometrical frustration were found [10]. The frustration parameter $f = -\theta_{CW}\, T_N^{-1}$, which is defined as the ratio of the negative Curie-Weiss temperature θ_{CW} and the ordering temperature T_N, gives a measure of the degree of frustration. Materials with $f > 10$ are considered to be strongly and materials with $f \approx 3$ are considered to be moderately frustrated. From susceptibility data we calculate a frustration parameter between 3 and 6 for $YbInNi_4$, i.e. $YbInNi_4$ is a moderately frustrated system. Finally we want to note that frustration will lead to finite entropy at low temperatures, implying that there is residual entropy in $YbInNi_4$ even below the ordering transition at 3 K. This could be a possible explanation for why at the ordering transition an entropy less than $R \ln 2$ is liberated although the CF ground state is most likely a Γ_8 quartet.

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