Magnetic Field Induced Orbital Polarization in Cubic $YbInNi_4$: Determining the Quartet Ground State Using X-Ray Linear Dichroism

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We have been able to induce a linear dichroic signal in the Yb M_5 x-ray absorption white line of cubic $YbInNi_4$ by the application of a magnetic field. The nonzero integrated intensity of the magnetic field induced dichroic spectrum indicates a net noncubic $4f$ orbital polarization. A quantitative analysis of the temperature and field strength dependence establishes that the crystal-field ground state is a Γ_8 quartet. The results demonstrate the potential of magnetic field induced linear dichroism as a new powerful approach for the investigation of the degeneracy and orbital degrees of freedom of cubic heavy-fermion and Kondo systems.

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We have recently shown that polarization dependent soft x-ray absorption spectroscopy (XAS) at the rare-earth $M_{4,5}$ edges is a very powerful method to determine the crystal-field (CF) ground state wave function of tetragonal $4f$ Kondo and heavy-fermion systems [1–3]. It provides valuable information complementary to neutron scattering experiments.

In this study we would like to explore the possibilities to also apply XAS for *cubic* $4f$ systems, a class of materials with quite intriguing properties [4–22]. At first sight, one does not expect any polarization dependence since a cubic wave function is isotropic for a dipole allowed transition process and, consequently, one would not expect to gain insight about the question of which of the cubic wave functions actually forms the ground state. However, here we demonstrate that the application of a magnetic field can provide key information about the nature of the ground state wave function. We have done so using $YbInNi_4$ as an exemplary model system: it has the relative simplicity of a stable valent system and yet there is a long-standing debate about its ground state wave function [23–25]. Very recently, a new interesting scenario has also been proposed for the closely related compound $Yb_{0.5}Y_{0.5}InCu_4$ [26]. We will show that the ground state of $YbInNi_4$ is a quartet. Our results demonstrate that—in addition to neutron [7,12] and (resonant) x-ray scattering [9–11,13]—we have a new approach for the determination of the degeneracy and orbital degrees of freedom in cubic rare-earth systems, which is important for the modeling of the properties of many of the Kondo insulators [4] as well as of the fascinating phenomena occurring in, for instance, the large group of skutterudite compounds, which includes metal-to-insulator transitions, superconductivity, and multipolar order or disorder [14–22].

The static susceptibility of $YbInNi_4$ shows a Curie-Weiss behavior with nearly the full Yb^{3+} moment down to about 3 K where it orders magnetically [24]. In the cubic C15b structure of $YbInNi_4$ the eightfold degenerate Hund's rule ground state of Yb^{3+} with $J = 7/2$ splits in cubic site symmetry into two doublets $|\Gamma_6\rangle$ and $|\Gamma_7\rangle$ and one quartet $|\Gamma_8\rangle$ which can be written in a $|J_z\rangle$ basis as

$$
\begin{aligned}
|\Gamma_6\rangle &= \begin{cases} c'|-7/2\rangle + d'|+1/2\rangle \\ c|+7/2\rangle + d|-1/2\rangle \end{cases}\\
|\Gamma_7\rangle &= \begin{cases} a'|-5/2\rangle - b'|+3/2\rangle \\ a|+5/2\rangle - b|-3/2\rangle \end{cases}\\
|\Gamma_8\rangle &\begin{cases} |\tilde{\Gamma}_6\rangle = \begin{cases} d'|-7/2\rangle - c'|+1/2\rangle \\ d|+7/2\rangle - c|-1/2\rangle \end{cases}\\ |\tilde{\Gamma}_7\rangle = \begin{cases} b'|-5/2\rangle + a'|+3/2\rangle \\ b|+5/2\rangle + a|-3/2\rangle \end{cases} \end{cases}
\end{aligned} \quad (1)
$$

with $a^2 + b^2 = a'^2 + b'^2 = c^2 + d^2 = c'^2 + d'^2 = 1$. Here a more general expression is chosen which holds in the presence of an applied magnetic field; i.e., it shows how states are modified by an applied magnetic field. For cubic site symmetry and no applied field, $a = a'$, $b = b'$ $c = c'$, and $d = d'$ is valid and $a = \sqrt{3/4}$ and $c = \sqrt{5/12}$, so that the CF problem reduces to determining which one of the three states forms the ground state [27].

$YbInNi_4$ is a good example for how different techniques can yield different CF results. Figure 1 summarizes some

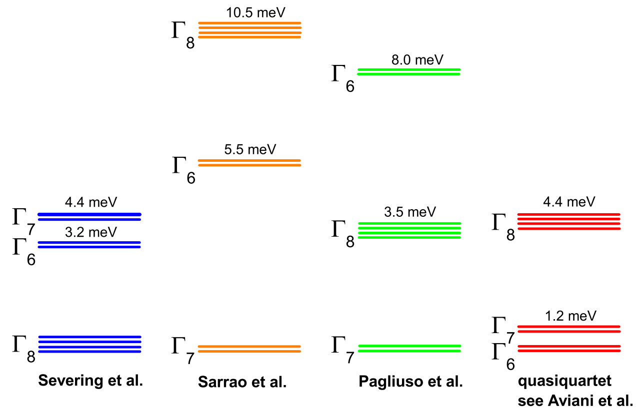

FIG. 1 (color online). Crystal-field schemes as published in [23–26].

crystal-field scenarios which have been suggested for this system: inelastic neutron scattering studies infer a $|\Gamma_8\rangle$ quartet ground state [23], while specific heat, magnetization, and ESR experiments claimed to have found a $|\Gamma_7\rangle$ doublet ground state [24,25]. Yet, one can envision even another scenario: measurements on $YbInCu_4$ with 50% Y doping proposed a CF scheme with a quasiquartet ground state as shown on the right-hand side in Fig. 1 [26]. Here we note that the crystal-field scheme in $YbInNi_4$ and the high temperature phase of the $YbInCu_4$ system are commonly regarded as being very similar [28].

Figure 2 displays the $4f$ angular hole distributions of the $|\Gamma_6\rangle$, $|\Gamma_7\rangle$, and $|\Gamma_8\rangle$ CF states (upper panel, from left to right) of the Yb $4f^{13}_{7/2}$ multiplet in cubic symmetry. We also calculate the corresponding $3d \rightarrow 4f$ XAS, which all consist of one single line: 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 $4f$ spin-orbit interaction. None of these CF states show a polarization dependence for linearly polarized x rays coming in with the electric field vector **E** parallel (red) or perpendicular (blue dashed) to the [001] crystallographic axis.

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 $|\Gamma_8\rangle$ state becomes split into the $|\tilde{\Gamma}_6\rangle$ and $|\tilde{\Gamma}_7\rangle$ states. While the $4f$ spatial distribution of the $|\Gamma_7\rangle$ and $|\Gamma_6\rangle$ does not change, that of the $|\Gamma_8\rangle$ is transformed into quite different looking spatial distributions of the $|\tilde{\Gamma}_6\rangle$ and $|\tilde{\Gamma}_7\rangle$ states, respectively. This is shown in the lower panel of Fig. 2. It is important to note that the spatial distributions of the $|\tilde{\Gamma}_6\rangle$ and $|\tilde{\Gamma}_7\rangle$ are *not* cubic. Consequently, there will be a linear polarization dependence in the XAS for these two states as also illustrated in Fig. 2: the so-called magnetic field induced linear dichroic (MILD) signal, i.e., the magnetic field induced difference of the absorption between linearly polarized

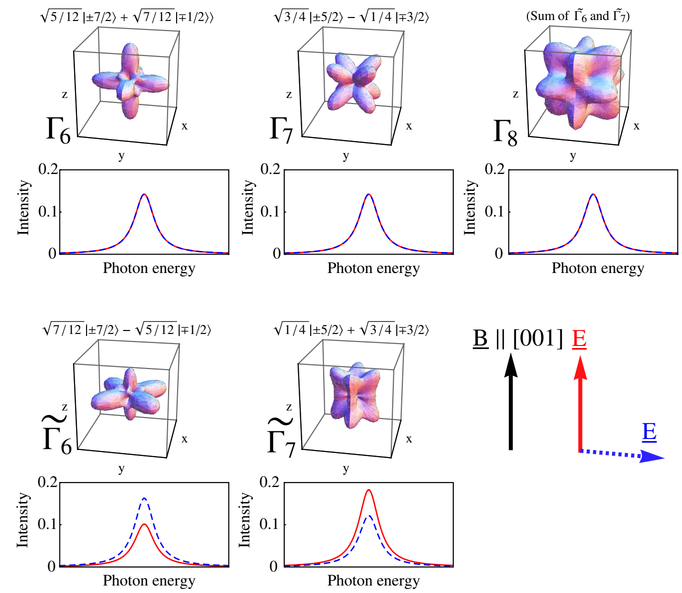

FIG. 2 (color online). Angular hole distributions and their corresponding polarization dependent M_5 XAS spectra of the $4f^{13}_{7/2}$ wave functions in cubic symmetry. The upper panels show the distributions and spectra in the absence of an external field. The lower panels display the decomposition of the $|\Gamma_8\rangle$ distribution in the presence of magnetic field into the $|\tilde{\Gamma}_6\rangle$ and $|\tilde{\Gamma}_7\rangle$ [see Eq. (1)], together with their corresponding spectra. The orientation of the applied magnetic field and electric field vector **E** of the linearly polarized light relative to the [001] crystallographic axis is also depicted.

x rays coming in with the electric field vector **E** parallel (red) or perpendicular (blue dashed) to the [001] crystallographic axis, is significant. The MILD signals of these two states are equally large but have opposite signs as the sum must vanish.

A polarization dependent XAS experiment in a magnetic field can therefore give a simple yes or no answer to the question of whether the ground state in a cubic material is a quartet or a doublet [29]. Yet, the above-mentioned analysis is valid for CF splittings very much larger than the Zeeman splitting. For the $YbInNi_4$ system, the CF splittings could be of the same order of magnitude as the Zeeman splitting: the CF energies are about 4 meV and the Zeeman splitting amounts to 0.5–1.0 meV when a 5 T field is applied. The cubic wave functions are then no longer eigenstates of the system, and all states, doublets and quartets, will give rise to a polarization dependence in the XAS. A quantitative analysis needs to include all these effects as is done in the following sections.

The XAS measurements were performed at the ID08 beam line of the ESRF. The photon energy resolution at the Yb M_5 edge ($h\nu \approx 1520$ eV) was set at ≈ 1.4 eV. The magnetic field is applied perpendicular to the Poynting vector of the light. The electric field vector **E** of the linearly polarized light can be switched between parallel and perpendicular to the magnetic field, and the degree of linear polarization was ≈ 99%. The spectra were recorded using the total electron yield method in an ultrahigh-vacuum chamber with a base pressure of 5×10^{-10} mbar. Clean sample areas were obtained by cleaving two $YbInNi_4$ crystals *in situ*. The (100) cleavage surface was set 5° off the magnetic field direction in order to avoid the Lorenz force hindering the electrons from escaping the sample surface. The temperature was measured using a certified Lake Shore Cernox thermoelement on the sample holder 5 mm above the sample, and the temperature gradient on the sample holder had been calibrated before the experiment.

Figure 3 shows the x-ray absorption spectra of $YbInNi_4$ at the Yb M_5 edge for the electric field vector **E** parallel and perpendicular to the magnetic field which is oriented close to the [001] crystallographic axis. The measurements were carried out with the sample at 6.5 ± 0.5 K for fields up to 5 T. The magnetic field clearly induces a significant polarization dependence. For a quantitative analysis, we now define the magnetic field induced linear dichroism as MILD $= (I_\perp - I_\parallel)/(2I_\perp + I_\parallel)$, where $I_\parallel$ and $I_\perp$ are the integrated absorption intensities for light polarized parallel and perpendicular to the magnetic field.

To interpret the data, we start with the remark that the linear dichroisms for the pure $|J_z\rangle$ states are -0.357 for $|1/2\rangle$, -0.214 for $|3/2\rangle$, $+0.071$ for $|5/2\rangle$, and $+0.500$ for $|7/2\rangle$. At 0 K and in the limit that the Zeeman splitting is much smaller than the CF splittings, the MILD for the cubic states [$a = \sqrt{3/4}$ and $c = \sqrt{5/12}$ in Eq. (1)] are zero for the $|\Gamma_6\rangle$ and $|\Gamma_7\rangle$, and $+0.143$ for the $|\tilde{\Gamma}_6\rangle$ of the Zeeman split $|\Gamma_8\rangle$ manifold. Note that the $|\tilde{\Gamma}_6\rangle$ forms the lowest state. Taking into account the thermal occupation of the states at 6.5 K and 5 T, the MILD for the $|\Gamma_8\rangle$ manifold reduces to $+0.038$ because now the $|\tilde{\Gamma}_7\rangle$ contributes to the dichroism with the opposite sign.

For $YbInNi_4$ we have to consider the CF energies as proposed in the scenarios displayed in Fig. 1. We have calculated the corresponding MILD as a function of magnetic field. The results for 0 K are shown in the top panel of Fig. 4. For infinitesimally small (nonzero) magnetic fields, only the Severing scenario produces a MILD with the $+0.143$ value mentioned above. Its MILD value increases steadily with rising magnetic fields because the lowest Zeeman state $|\tilde{\Gamma}_6\rangle$ of the $|\Gamma_8\rangle$ manifold gains more $|J_z\rangle = |7/2\rangle$ character due to the energy lowering of the latter by the magnetic field; i.e., in Eq. (1) the d coefficient increases and the d' decreases for positive external fields. This is very effective to create an increase in the MILD since this $|7/2\rangle$ carries the largest LD of all pure $|J_z\rangle$ states. The amount of increase of the MILD (and the $|7/2\rangle$ character) with field depends inversely on the magnitude of the CF splitting between the $|\tilde{\Gamma}_6\rangle$ and $|\Gamma_6\rangle$.

The Aviani scheme also produces MILD but with smaller values: the MILD vanishes for small fields, and it increases almost linearly with increasing field for a similar reason as in the Severing scenario: the $|J_z\rangle = |7/2\rangle$

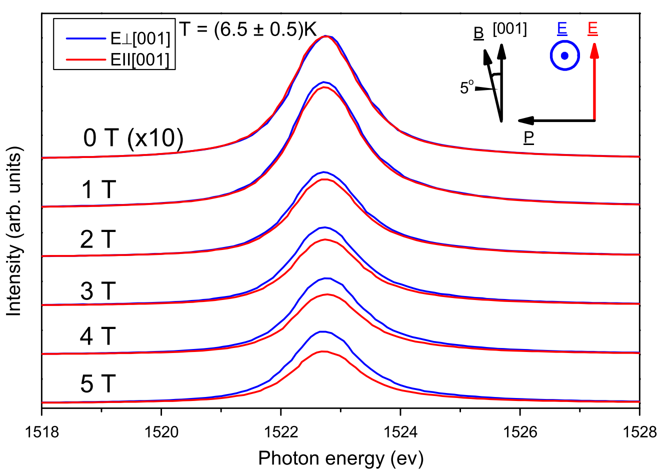

FIG. 3 (color online). Experimental x-ray absorption spectrum of $YbInNi_4$ at the Yb M_5 edge for linearly polarized light coming in with the electric field vector **E** parallel [light (red) lines] and perpendicular [dark (blue) lines] to the magnetic field oriented close to the [001] crystallographic axis.

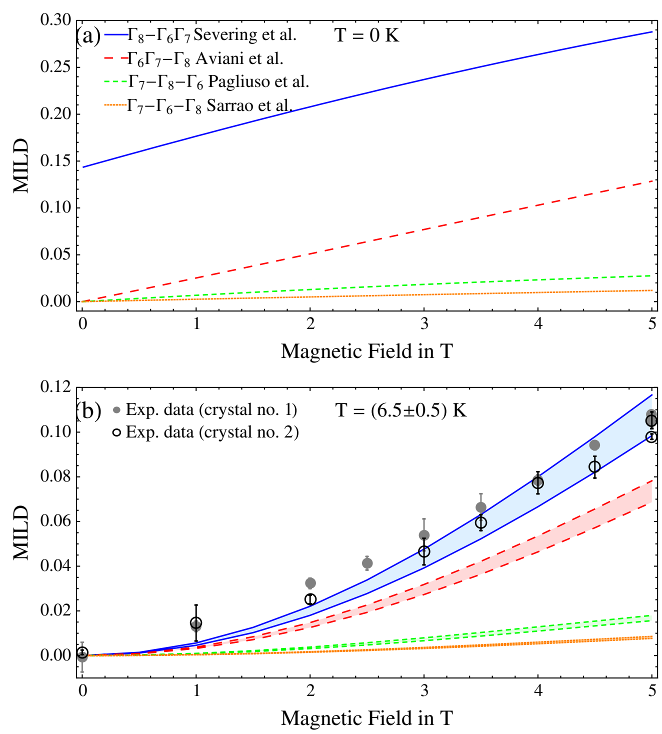

FIG. 4 (color online). Magnetic field induced linear dichroism (MILD) as a function of magnetic field calculated using the CF scheme of Severing *et al.* [23] (blue line), Sarrao *et al.* [24] (orange line), Pagliuso *et al.* [25] (green dotted line), and Aviani *et al.* [26] (red dashed line), at 0 K (top panel) and for the temperature range between 6 and 7 K (6.5 ± 0.5 K) (bottom panel). The open and full circles in the bottom panel correspond to the measurements of two different $YbInNi_4$ crystals.

component increases in the lowest state, which is here the $|\Gamma_6\rangle$. This is described by an increase of the c coefficient and a decrease of the c' in Eq. (1) for a positive field. The slope of MILD versus field is almost identical as for the Severing scenario since the energy splitting is almost the same. The Sarrao and Pagliuso scenarios produce hardly any MILD even at large magnetic fields due to the fact that the $|3/2\rangle$ and $|5/2\rangle$ components in the $|\Gamma_7\rangle$ lowest state already carry by themselves smaller LD signals, so that the redistribution of their relative weights due to the magnetic field has little effect on the net LD.

The top panel of Fig. 4 reveals clearly that at 0 K the experiment should be performed at low fields in order to obtain optimum contrast between the Severing scenario on one hand and the other scenarios on the other hand, and at the highest possible field to distinguish the Aviani scheme from the Sarrao and Pagliuso one. In practice, 6.5 K was the lowest possible temperature which we could reach. This then changes the situation and the bottom panel of Fig. 4 displays the expected MILD for the four different scenarios for a temperature in the range between 6 and 7 K. The thermal population of the next higher Zeeman states reduces the MILD considerably, especially for the Severing scenario. Yet, the distinction between the scenarios is still large for high magnetic fields.

We now plot in the lower panel of Fig. 4 the experimental MILD at 6.5 ± 0.5 K as a function of field: it is zero for 0 T and increases to about 10.5% for 5 T. The open and full circles correspond to the two crystals, both measured twice at 5 T, once straight after cleaving and once after all the runs with different fields strengths were completed. The MILD has been determined from at least 10 scans measured in sequences of parallel-perpendicular-perpendicular-parallel polarization and then averaged. One can observe that the Severing scenario fits well to the experimental data. The Aviani scheme, on the other hand, provides MILD values which are about 30% lower, a significant discrepancy. The Sarrao and Pagliuso scenarios can clearly be ruled out since the expectation values are much smaller than the measured ones.

We therefore conclude from our MILD measurements that the $|\Gamma_8\rangle$ is the only possible ground state wave function. This is consistent with the findings of recent magnetic form factor experiments [30]: the measured spatial distribution of the $4f$ magnetic moment also rules out $|\Gamma_7\rangle$ as ground state, but cannot distinguish between the $|\Gamma_6\rangle$ and $|\Gamma_8\rangle$ scenarios.

To summarize, we have demonstrated in simulations and experiment that a MILD in an x-ray absorption experiment at the $3d \rightarrow 4f$ edge can give information about the ground state wave function of a rare-earth cubic compound. We have further shown that in the event of comparable Zeeman and CF energies the MILD can still give a unique result when the sample temperature is sufficiently low and well defined. The measured MILD in $YbInNi_4$ can only be explained with a $|\Gamma_8\rangle$ quartet ground state.

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