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Crystal field study in rare-earth-doped LuInNi₄

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Magnetic susceptibility and electron spin resonance experiments in the rare earth (R = Nd, Er, and Yb) 5–25% doped cubic intermetallic LuInNi₄ enable estimates of the fourth A₄ and sixth A₆ order crystal-field parameters for this compound. These parameters yield a Γ₉ doublet, a Γ₆ doublet, and a Γ₄ quartet as the ground states for Nd³⁺, Er³⁺, and Yb³⁺, respectively, and an overall crystal-field splitting of 100–300 K. The A₄ and A₆ parameters are found to have comparable order of magnitude for all the R studied and their values are in agreement with reported values for other cubic systems.

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I. INTRODUCTION

The series of intermetallic compounds YbA(Cu,Ni)₄ (A = transition metal) have been extensively studied since the discovery of the first-order isostructural phase transition at Tᵦ≈40 K in the intermediate valence compound YbInCu₄.1 Extensive studies2 of susceptibility, specific heat, resistivity, Yb Mossbauer, lattice parameter, LIII x-ray absorption, and NMR3,4 are consistent with a=0.45% volume expansion below Tᵦ, and an Yb valence change from z≈2.9 above to z≈2.8 below Tᵦ.4 This material forms in the cubic AuBe₅ (C15b,F43m)-type structure5 and, as other isomorphic Yb-based variants, it has interesting properties resulting from the interplay among Kondo effect, crystal-field effects (CFE), and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions.6 YbAgCu₄, for example, has a relatively large linear coefficient of specific heat (γ≈240 mJ/mol K²),7,8 and a temperature-dependent magnetic susceptibility with a maximum at ≈ 35 K (Ref. 7) that can be described by the Bethe-ansatz solution of the Coqblin-Schrieffer Hamiltonian.7,10,11 The crystalline electric-field splitting in this compound appears to be comparable to the spin-fluctuation temperature and consequently does not significantly influence the ground state.7–13 In contrast, CFE and the RKKY interactions are dominant for YbAuCu₄, YbPdCu₄, and YbInCu₄.6,12,13 YbInCu₄ is particularly interesting due to its ferromagnetic order near 3 K, a relatively unusual ground state for trivalent Yb compounds.13 Resistivity, specific heat, and magnetization measurements13 are consistent with a doublet ground state for Yb³⁺ in YbInCu₄ and fits to magnetization data yield Lea, Leask, Wolf (LLW) parameters of x=0.53 and W=0.48 meV.13 However, earlier neutron-scattering results suggested a quartet ground state for Yb³⁺ in YbInCu₄.14 The LLW values, x=0.53 and W=0.48 meV of Ref. 13, yield crystalline electric-field parameters that would predict a Γ₉ ground state for Nd³⁺ in the same crystal-field environment, whereas a Γ₆ doublet ground state has been observed in electron spin resonance (ESR) experiments for Nd³⁺ in LuInNi₄.15 Because the crystal-field scheme, and associated ground-state degeneracy, is important for guiding the interpretation of the low-T properties of these materials, we have performed further CFE investigations in rare-earth-doped LuInNi₄ in order to understand the role of CFE in YbInNi₄ and the different observation reported in Refs. 13 and 14. Rare-earth doping in a nonmagnetic reference compound has been used successfully for CFE studies in other cubic systems.16 In this work, we have studied the CFE in the Lu₁₋ₓRₓInNi₄ (R = Nd, Er, Yb, and 0.05≤ x ≤0.25) compounds. By means of ESR and magnetic susceptibility experiments, it has been possible to estimate the fourth (A₄) and sixth (A₆) order cubic crystal-field parameters (CFP) for these systems.

II. EXPERIMENT

Single-crystalline samples of the Lu₁₋ₓRₓInNi₄ (R = Nd, Er, Yb, and 0.05≤ x ≤0.25) compounds were grown from the melt in In-Ni flux as described previously.13 Typical crystal sizes were 2×2×2 mm³. The structure and phase purity were checked by x-ray powder diffraction, and the crystal orientation was determined by the usual Laue method. The ESR experiments were carried out in a conventional Bruker ESR spectrometer using a TE₀₁₀₂ room-temperature cavity. The sample temperature was varied using a helium gas-flux temperature controller. To increase the ESR signal to noise ratio, the T dependence of the spectra was taken in powdered samples. However, single crystals
were used to look for anisotropic effects. Magnetization measurements were made in a Quantum Design dc superconducting quantum interference device magnetometer.

### III. RESULTS AND DISCUSSION

Figure 1 shows the ESR powder spectra of Nd$^{3+}$ in Lu$_{0.75}$Nd$_{0.25}$InNi$_4$, measured at $T=4.0$ K. As previously reported for the more diluted samples, $15$ isotropic resonance with typical Dysonian line shapes $[A/B=2.2(2)]$ are observed. These line shapes are characteristic of localized magnetic moments in a metallic host with a skin depth smaller than the size of the sample particles. The $g$ value and linewidth $D_H$ were obtained by fitting the resonance to the appropriate admixture of absorption and dispersion.$^{17,18}$ The solid line, in Fig. 1, is the best fit to the observed resonance and gives $g=2.60(2)$ and $D_H=170(30)$ G. As previously reported for more diluted samples in Ref. 15, the intensity of the resonance increases as the temperature decreases. Therefore the $g=2.60(2)$ observed isotropic resonance is a strong evidence of a $G_6$ doublet ground state of the crystal-field splitted Nd$^{3+}$ $J=9/2$ multiplet. Esr spectra associated with the others two quartets ($T_5^1$ and $T_5^2$) (Ref. 19) of the crystal-field splitted Nd$^{3+}$ $J=9/2$ multiplet usually present strongly anisotropic linewidths and/or $g$ values. $^{20}$ The hyperfine lines of the two Nd isotopes with nonzero nuclear spin reported in Ref. 15 cannot be observed in the presented data probably due to inappropriate experimental conditions (resolution and field range) and/or a broader character of the lines (Fig. 1 and Ref. 15).

The temperature dependence of the linewidth for Nd$^{3+}$ in Lu$_{0.75}$Nd$_{0.25}$InNi$_4$ is plotted in Fig. 2. The expected linear dependence (Korringa rate$^{21}$ of the linewidth was fitted to the expression $D_H=a+bT$. A linear thermal broadening of the linewidth indicates that the spin relaxation process is mainly given by the interaction between the localized 4$f$ electron and the conduction electrons. Within the accuracy of the measurements, the $g$ values are temperature independent. The $a$, $b$, and $g$ parameters agree, within our experimental error, with the values reported earlier for more diluted Nd$^{3+}$ samples. $^{15}$ Their values are shown in Table I. This result and the absence of ESR resonance linewidth broadening at low $T$ (see Fig. 2) for Nd$^{3+}$ in Lu$_{0.75}$Nd$_{0.25}$InNi$_4$ indicates that even for these levels of rare-earth concentration we may neglect the coupling between the rare earths in the analysis of the susceptibility data.

### TABLE I. Experimental parameters for $R$InNi$_4$.

<table>
<thead>
<tr>
<th>$R$</th>
<th>$g$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$W$</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:LuInNi$_4$</td>
<td>2.61(2)$^a$</td>
<td>93(10)$^a$</td>
<td>30(6)$^a$</td>
<td>0.03(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd:LuInNi$_4$</td>
<td>2.60(2)</td>
<td>170(30)$^a$</td>
<td>40(8)$^a$</td>
<td>0.25 nominal</td>
<td>3.50(5)</td>
<td>0.15(3)</td>
</tr>
<tr>
<td>Yb:LuInNi$_4$</td>
<td>0.10 nominal</td>
<td>-4.18(5)</td>
<td>-0.81(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er:LuInNi$_4$</td>
<td>0.10 nominal</td>
<td>-0.23(3)</td>
<td></td>
<td>0.09(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YbInNi$_4$</td>
<td>$\approx 5.6$ K (0.48 meV)$^a$</td>
<td></td>
<td></td>
<td>$\approx 0.53^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YbInNi$_4$</td>
<td>$\approx -2.0$ K (-0.17 meV)$^b$</td>
<td></td>
<td></td>
<td>$\approx 0.38^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$See Ref. 13.
$^b$See Ref. 14.
Curie-Weiss temperatures, \( u \)

The high shows

\( R \)

Hamiltonian

samples. The solid lines are the best fit to the data using the

\( u \)

where the

\( B_n \)

that includes the cubic crystal-field and Zeeman terms. The

\( J \)

Hence the magnetic susceptibility is given by

\( E_n \)

cally the Hamiltonian we get the eigenvalues

\( B_n \)

operators, respectively.

\( B_n \)

crystal-field terms in the Hamiltonian. The Yb\(^{3+}\) crystal field split-

\( x' \)

ted ground-state multiplet (\( J=7/2 \)) is shown.

Figure 3 presents the temperature and field dependence of the

\( u \)

the inverse magnetic susceptibility, \( x \)

\( 10,50 \) kOe

2

\( O_n \)

\( 0 \)

\( 1 \)

\( 4 \)

\( 1 \)

\( 2 \)

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The crystal-field scheme of levels obtained for Yb, Er, and Nd is consistent with a stronger low-temperature magnetic-field dependence in $\chi(T)$ for Yb and Er. This is because their low-temperatures crystal-field levels and much closer to each other than in the Nd case, and a few Kelvins introduced by magnetic field can affect their low-temperature magnetic susceptibility. In addition, one should expect larger deviation from the linear Curie behavior for the Nd case, because the overall crystal-field splitting is bigger (340 K) for Nd.

Magnetic susceptibility and ESR experiments in rare-earth (R = Nd, Er, and Yb)-doped LuInNi$_4$ allowed us to estimate the $A_4$ and $A_6$ CFP for this compound. The $A_4$ and $A_6$ CFP obtained for Er$^{3+}$, Nd$^{3+}$, and Yb$^{3+}$ in LuInNi$_4$ are of the same order of magnitude as those reported for rare earths in other cubic materials. The sign and order of magnitude of the $A_4$ and $A_6$ CFP are also similar for Er$^{3+}$, Nd$^{3+}$, and Yb$^{3+}$ in LuInNi$_4$. We should mention that the LLW parameters given in Ref. 13 lead to a sign and value for $A_4$ and to an overall crystal-field splitting which are in good agreement with those obtained for our Yb-doped LuInNi$_4$ (see Table II). In both cases the ground state for Yb$^{3+}$ is a $\Gamma_7$ doublet. However, the positive sign of $A_6$, obtained from the LLW parameter given in Ref. 13, would predict a different ground state than that observed for Nd$^{3+}$ in our ESR experiments. Therefore, for the doping levels of the studied samples, our results for Yb$^{3+}$ in LuInNi$_4$ are closer to those reported in Ref. 13. The difference in sign for $A_6$ (see Table II) is probably associated to small differences in the lattice parameter and/or to a different electronic structure in YbInNi$_4$ ($\gamma = 150$ m$^3$/mol K$^2$). On the other hand, the LLW parameters reported in Ref. 14 yield a positive value for $A_4$, a smaller overall splitting ($\approx 50$ K), and a $\Gamma_8$ quartet ground state for Yb$^{3+}$ in YbInNi$_4$. These results do not agree with the $A_4$ values found in this work and with that obtained from resistivity, specific-heat, and magnetization measurements (see Ref. 13). The reason for the discrepancy between the neutron-scattering results given in Ref. 14 and the other crystal-field related data reported in the literature are still not understood. Further neutron studies in YbInNi$_4$, as well as studies of the evolution of the $A_4$ and $A_6$ CFP as a functions of the lattice parameters and/or electronic structure of the (Lu,Yb)InNi$_4$ system, would probably help to elucidate the discrepancies.

Finally, we should mention that we have not observed the Er$^{3+}$ and Yb$^{3+}$ resonance in our samples. The absence of these resonance is probably associated with the highly anisotropic character and fast relaxation of the $\Gamma_8$ ground state in the Er case and with the local enhancement of the density of the states for the Yb case. These effects can produce strong broadening of the ESR spectra.

IV. CONCLUSIONS

In summary, the CFP $A_4$ and $A_6$ in Lu$_{1-x}$R$_x$InNi$_4$ (0.05 $\leq x \leq 0.25$), for the non-$S$-state ions, $R$ = Nd$^{3+}$, Er$^{3+}$, and Yb$^{3+}$, were determined from magnetic susceptibility and ESR experiments. The $A_4$ and $A_6$ CFP have the same sign and comparable order of magnitude, suggesting that, for
these level of doping, rare-earth-doped samples allow the estimation of the LuInNi₄ CFP with good accuracy. The obtained sign and values of $A_4$ and the overall splitting for Yb¹⁺ in YbInNi₄ were found to be in very good agreement with those extracted from the LLW parameters reported in Ref. 13. Thus rare-earth doping in a nonmagnetic reference compound is a convenient way to study CFE in cubic magnetic systems.

ACKNOWLEDGMENTS

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