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Crystal field study in rare-earth-doped LuInNi$_4$

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Magnetic susceptibility and electron spin resonance experiments in the rare earth ($R = \text{Nd, Er, and Yb}$) 5–25% doped cubic intermetallic LuInNi$_4$ enable estimates of the fourth $A_4$ and sixth $A_6$ order crystal-field parameters for this compound. These parameters yield a $\Gamma_6$ doublet, a $\Gamma_7$ doublet, and a $\Gamma_8$ quartet as the ground states for Nd$^{3+}$, Er$^{3+}$, and Yb$^{3+}$, respectively, and an overall crystal-field splitting of 100–300 K. The $A_4$ and $A_6$ 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 $T_\text{v} = 40$ K in the intermediate valence compound YbInCu$_4$. Extensive studies of susceptibility, specific heat, resistivity, Yb Mossbauer, lattice parameter, $L_{III}$ x-ray absorption, and NMR are consistent with a $\Delta$ at 0.45% volume expansion below $T_\text{v}$, and an Yb valence change from $z = 2.9$ above to $z = 2.8$ below $T_\text{v}$. This material forms in the cubic AuBe$_5$ ($C15b, F43m$)-type structure 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. YbAgCu$_4$, for example, has a relatively large linear coefficient of specific heat ($\gamma = 240$ mJ/mol K$^2$), and a temperature-dependent magnetic susceptibility with a maximum at $\approx 35$ K (Ref. 7) that can be described by the Bethe-ansatz solution of the Coqblin-Schrieffer Hamiltonian. 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. In contrast, CFE and the RKKY interactions are dominant for YbAuCu$_4$, YbPdCu$_4$, and YbInAl$_4$, and YbInNi$_4$ is particularly interesting due to its ferromagnetic order near 3 K, a relatively unusual ground state for trivalent Yb compounds. Resistivity, specific heat, and magnetization measurements are consistent with a doublet ground state for Yb in YbInNi$_4$ and fits to magnetization data yield Lea, Leak, Wolf (LLW) parameters of $x = 0.53$ and $W = 0.48$ meV. However, earlier neutron-scattering results suggested a quartet ground state for Yb in YbInNi$_4$. The LLW values, $x = 0.53$ and $W = 0.48$ meV of Ref. 13, yield crystalline electric-field parameters that would predict a $\Gamma_8$ ground state for Yb$^{3+}$ in the same crystal-field environment, whereas a $\Gamma_6$ doublet ground state has been observed in electron spin resonance (ESR) experiments for Yb$^{3+}$ in LuInNi$_4$. 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 LuInNi$_4$ in order to understand the role of CFE in YbInNi$_4$ and the different observation reported in Refs. 13 and 14. Rare-earth doping in a nonmagnetic reference compound has been successfully used for CFE studies in other cubic systems. In this work, we have studied the CFE in the Lu$_{1-x}R_x$InNi$_4$ ($R = \text{Nd, Er, Yb, and } 0.05 \leq x \leq 0.25$) compounds. By means of ESR and magnetic susceptibility experiments, it has been possible to estimate the fourth ($A_4$) and sixth ($A_6$) order cubic-crystal-field parameters (CFP) for these systems.

II. EXPERIMENT

Single-crystalline samples of the Lu$_{1-x}R_x$InNi$_4$ ($R = \text{Nd, Er, Yb, and } 0.05 \leq x \leq 0.25$) compounds were grown from the melt in In-Ni flux as described previously. Typical crystal sizes were $2 \times 2 \times 2$ mm$^3$. 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 TE$_{102}$ 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

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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$_{1-x}$Nd$_x$InNi$_4$ (x = 0.25 nominal) at $T = 4.8$ K. The solid line is the best fit of the resonance with a Dyson line shape.

The temperature dependence of the linewidth for Nd$^{3+}$ in Lu$_{1-x}$Nd$_x$InNi$_4$ (x = 0.25 nominal) is plotted in Fig. 2. The expected linear dependence (Korringa rate) of the linewidth was fitted to the expression $D_H = a + bT$. $a$ and $b$ are given in Table I.

| TABLE I. Experimental parameters for RInNi$_4$. |
|---|
| R | $g$ | $a$ | $b$ | $c$ | $W$ | $x$ |
|---|
| Nd:LuInNi$_4$ | 2.61(2)$^a$ | 93(10)$^a$ | 30(6)$^a$ | 0.03(5) |
| Nd:LuInNi$_4$ | 2.60(2) | 170(30)$^a$ | 40(8)$^a$ | 0.25 nominal | 3.50(5) | 0.15(3) |
| Yb:LuInNi$_4$ | 0.10 nominal | -4.18(5) | -0.81(3) |
| Er:LuInNi$_4$ | 0.10 nominal | -0.23(3) | 0.09(5) |
| YbInNi$_4$ | $\approx 5.6$ K (0.48 meV)$^a$ | $\approx 0.53$ |
| YbInNi$_4$ | $\approx -2.0$ K (-0.17 meV)$^b$ | $\approx 0.38$ |

$^a$See Ref. 13.
$^b$See Ref. 14.
FIG. 3. Temperature and field dependence of the inverse magnetic susceptibility, \( \chi^{-1}(T, H = 1.5 \text{ T}) \) for \( \text{Lu}_{0.9}\text{Yb}_{0.1}\text{InNi}_4 \) single crystal. The inset shows the free ion inverse susceptibility, \( \chi^{-1} \). The solid lines are the best fit to the data of the calculated susceptibility including the Zeeman and LLW cubic crystal-field terms in the Hamiltonian. The Yb\(^{3+} \) crystal field split-off ground-state multiplet \( (J = 7/2) \) is shown.

Figure 3 presents the temperature and field dependence of the inverse magnetic susceptibility, \( \chi^{-1}(T, H = 10.50 \text{ kOe}) \) for \( \text{Lu}_{0.9}\text{Yb}_{0.1}\text{InNi}_4 \) crystals. The inset shows (straight line) the free-ion inverse susceptibility, \( \chi^{-1} \). The high \( T (T \approx 250 \text{ K}) \) susceptibility gives very small Curie-Weiss temperatures, \( |\theta_p| \approx 5 \text{ K} \). This also indicates that \( R-R \) impurities interactions are negligible for the studied samples. The solid lines are the best fit to the data using the Hamiltonian

\[
H = B_n[O_n^0 + 5O_n^4] + B_n[O_n^0 - 21O_n^2] + g_J \mu_B \vec{H} \cdot \vec{J}
\]

that includes the cubic crystal-field and Zeeman terms. The \( B_n \) and \( O_n^m \) are the \( n \)-th order CFP and equivalent Stevens operators, respectively. \( B_n = A_n (r^n) \theta_p \), \( g_J \) is the Landé factor and \( \mu_B \) is the Bohr magneton.\(^9 \) Diagonalizing numerically the Hamiltonian we get the eigenvalues \( E_n \) and corresponding eigenfunctions that can be written as

\[
|\phi_n\rangle = \sum_{M=-J}^{J} C_M^n |JM\rangle,
\]

where the \( |JM\rangle \) expand the manifold of angular momentum \( J \). Hence the magnetic susceptibility is given by

\[
\chi = \frac{g_J \mu_B \sum_n \exp \left( -\frac{E_n}{kT} \right) \sum_{M=-J}^{J} |C_M^n|^2 M}{H \sum_n \exp \left( -\frac{E_n}{kT} \right)}.
\]

Defining the LLW parameters \( x \) and \( W \) by the equations\(^{19} \)

\[
B_4 F(4) = W x, \quad (4)
\]

\[
B_6 F(6) = W (1 - |x|), \quad (5)
\]

where \( F(4) \) and \( F(6) \) are scaling factors appropriate for each \( J \) value, we perform a least-squares fitting of the susceptibility leaving \( x \) and \( W \) as adjustable parameters. The fitting for Yb\(^{3+} \) in LuInNi\(_4\) leads to the LLW parameters, \( x = -0.81(3) \) and \( W = -4.18(5) \). These parameters predict a \( \Gamma_7 \) ground state, a \( \Gamma_8 \) first excited state at 45(5) K, and a \( \Gamma_6 \) second excited state at 115(8) K (see Fig. 3). The obtained \( \Gamma_7 \) doublet ground state for Yb\(^{3+} \) in LuInNi\(_4\) agrees with the specific-heat and resistivity data reported in Ref. 13 for YbInNi\(_4\). It is reasonable to assume that the cubic CFP, \( A_4 \) and \( A_6 \), at the R site in Lu\(_{1-x}\)R\(_x\)InNi\(_4\) \((R = \text{Yb, Nd, Er})\) would not be strongly affected by the R impurities. Therefore the ratio \( A_4/A_6 \) and the signs of \( A_4 \) and \( A_6 \) should remain approximately the same for all \( R \). Therefore taking into account the ratio \( (r^4)/(r^6) \) for Yb\(^{3+} \) and Nd\(^{4+} \) (Ref. 19), and using the obtained values of \( x = -0.81(3) \) and \( W = -4.18(5) \) for Yb\(^{3+} \), we can predict \( x \approx 0.50 \) and \( W > 0 \) for Nd\(^{3+} \) in LuInNi\(_4\). These values of \( x \) and \( W \) yield a \( \Gamma_6 \) doublet ground state for Nd\(^{3+} \) in LuInNi\(_4\). \(^{19} \) The \( \Gamma_6 \) ground state for Nd\(^{3+} \), with a theoretical \( g \) value of 2.667 (Ref. 19), is consistent with the observed ESR spectra (see also Ref. 15). On the other hand, if we use the values of \( x = 0.53 \) and \( W = 0.48 \) meV reported in Ref. 13 for YbInNi\(_4\), we find \( x \approx -0.70 \) and \( W < 0 \) for Nd\(^{3+} \) in LuInNi\(_4\). These values yield a \( \Gamma_8 \) ground state\(^{10} \) for Nd\(^{3+} \) which disagrees with the ESR results.

FIG. 4. Temperature and field dependence of the inverse magnetic susceptibility, \( \chi^{-1}(T, H = 1.5 \text{ T}) \) for \( \text{Lu}_{0.75}\text{Nd}_{0.25}\text{InNi}_4 \) single crystal. The inset shows the free ion inverse susceptibility, \( \chi^{-1} \). The solid lines are the best fit to the data of the calculated susceptibility including the Zeeman and LLW cubic crystal-field terms in the Hamiltonian. The Nd\(^{3+} \) crystal field split-off ground-state multiplet \( (J = 9/2) \) is shown.
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$_4$ ($\gamma=150$ mJ/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 Δ₄ and the overall splitting for Yb⁴⁺ 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.

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