# Evolution of the magnetic properties in the antiferromagnet Ce<sub>2</sub>RhIn<sub>8</sub> simultaneously doped with Cd and Ir

D. S. Christovam<sup>®</sup>, <sup>1</sup>G. S. Freitas, <sup>1</sup>M. M. Piva<sup>®</sup>, <sup>1,2</sup>J. C. Souza<sup>®</sup>, <sup>1</sup>M. O. Malcolms<sup>®</sup>, <sup>1</sup>O. L. Canton<sup>®</sup>, <sup>3</sup>J. B. Leão, <sup>4</sup>

W. Ratcliff,<sup>4</sup> J. W. Lynn,<sup>4</sup> C. Adriano,<sup>1</sup> and P. G. Pagliuso<sup>1</sup>

<sup>1</sup>Instituto de Física "Gleb Wataghin," UNICAMP, Campinas-SP, 13083-970, Brazil

<sup>2</sup>Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany

<sup>3</sup>Instituto de Física Teórica, Universidade Estadual Paulista-UNESP, São Paulo-SP, 01140-070, Brazil

<sup>4</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

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We report the evolution of the magnetic properties of  $Ce_2Rh_{1-x}Ir_xIn_{8-y}Cd_y$  single crystals. In particular, for  $Ce_2Rh_{0.5}Ir_{0.5}In_{0.5}Ir_{0.5}In_{0.5}In_{0.5}In_{7.79}Cd_{0.21}$  ( $T_N = 4.2$  K), we have solved the magnetic structure of these compounds using single-crystal neutron magnetic diffraction experiments. Taking the magnetic structure of the  $Ce_2RhIn_8$  heavy-fermion antiferromagnet as a reference, we have identified no changes in the  $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$  magnetic wave vector; however, the direction of the ordered  $Ce^{3+}$  moments rotates toward the *ab* plane, under the influence of both dopants. By constraining the analysis of the crystalline electric field (CEF) with the experimental ordered moment's direction and high-temperature magnetic-susceptibility data, we have used a mean-field model with tetragonal CEF and exchange interactions to gain insight into the CEF scheme and anisotropy of the CEF ground-state wave function when Cd and Ir are introduced into  $Ce_2RhIn_8$ . Consistent with previous work, we find that Cd doping in  $Ce_2RhIn_8$  tends to rotate the magnetic moment toward the *ab* plane although its connection to the CEF overall splitting evolution for the y = 0 samples may not be straightforward. These findings may shed light on the origin of the disordered spin-glass phase on the Ir-rich side of the phase diagram and also indicate that the  $Ce_2MIn_8$  compounds may not follow exactly the same Rh-Ir CEF effects trend established for the CeMIn<sub>5</sub> compounds.

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### I. INTRODUCTION

The Ce<sub>m</sub>*M*In<sub>3m+2</sub> (M =Co, Rh, Ir; m = 1, 2) family of heavy-fermion (HF) intermetallic compounds present the Ce<sup>3+</sup> magnetic moments immersed in a conduction-electron sea which exhibits a variety of magnetic and electronic interactions, such as the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect. Both depend on the exchange interaction between the f electron and conduction electrons,  $J_{fs}$ , and are affected by the crystalline electric field (CEF) effects, allowing for parameters such as pressure and doping to tune these competing interactions. Such an interplay leads to intricate phase diagrams, making it a vast playground for studying magnetic order, disordered or glassy states, the onset of unconventional superconductivity (SC), and quantum critical phenomena [1].

These compounds are tetragonal relatives of the cubic CeIn<sub>3</sub>, since the layers of CeIn<sub>3</sub> are intercalated by *m* layers of *M*In<sub>2</sub> along the *c* axis [2]. The evolution of the physical properties of the Ce<sub>*m*</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>In<sub>3*m*+2</sub> alloys has been thoroughly investigated. Transport measurements under applied pressure and nuclear quadrupole resonance studies in the Ce-115 (m = 1) compounds have shown that in Rh-rich compounds the ground state (GS) tends to favor antiferromagnetic (AFM) states [3–5]. Doping with Ir leads the system from an incommensurate AFM state towards two different supercon-

ducting phases, which are favored by pressure tuning and are likely mediated by magnetic instabilities, despite their different origins [4,6,7]. It has been shown that for intermediate Ir concentrations the AFM state coexists with SC, going from an incommensurate order to commensurate order [5,8]. Such intricate properties sparked interest in the CEF scheme affecting the actual GS of the monolayered CeMIn<sub>5</sub> series [9–11]. Recent studies using inelastic-scattering techniques, with both x rays [x-ray absorption spectroscopy (XAS)] and neutrons [inelastic neutron scattering (INS)] [9,12,13], have probed the GS wave function of Ce-115 compounds, obtaining its admixing coefficients very precisely. These results revealed a GS dominated by flatter orbitals in CeRhIn<sub>5</sub>, which is the only magnetic Ce-115 at ambient pressure. Hence it is strongly suggested that the physical properties of the Ce-115 GS are driven by the single-ion anisotropy associated with the orbital distribution of  $Ce^{3+}$ .

The bilayered Ce<sub>2</sub>*M*In<sub>8</sub> (m = 2: Ce-218) compounds have also been studied under applied pressure [14]. Their structure is more three-dimensional-like than that of the Ce-115s as it encases a second CeIn<sub>3</sub> block and shows a Fermi surface slightly more tridimensional than that of their monolayered relatives [14,15]. For M = Rh, a superconducting dome was found as pressure suppresses the AFM order, inducing quantum fluctuations near a quantum critical point. Its magnetic structure at ambient pressure was determined through neutron diffraction, which found the magnetic moments to be lying at an angle of  $52^{\circ}$  from the *ab* plane [17]. In the case of the Rh-Ir alloys Ce<sub>2</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>In<sub>8</sub>, the Ir-rich compounds present a disordered state of random spin freezing below the transition temperature  $T_g$  resembling a spin-glass (SG) state, as well as a superconducting dome in the Ir-doping phase diagram, that can be suppressed by pressure [18,19]. Both superconducting states found in the Ce-218 compounds have lower critical temperatures than their Ce-115 analogs. However, their evolution with pressure is considerably different, and the origin and suppression of SC in the Ir-rich compounds remain unclear [18]. Growth reports of M = Co samples have shown SC below 0.4 K; however, the structural defects marked by the presence of spurious Ce-115 render these results unreliable [20,21].

Previous reports on Cd substitution in the In site showed that for Ce*M*In<sub>5</sub>, Cd tends to suppress superconducting states in M = Co, Ir while favoring AFM ordering for M = Rh[22,23]. Since Cd has one *p* electron fewer than In has, this dopant may suppress the hybridization strength between *f* and conduction electrons, ultimately tuning the ground state of the material [16,24]. Interestingly, the SC reemerges in the Cd-doped CeIrIn<sub>5</sub> under pressure, and recent neutrondiffraction studies on this compound provide evidence that the Ce<sup>3+</sup> magnetic moments lie along the structural *c* axis [7,25]. This magnetic structure is remarkably different from both magnetic structures presented by CeRhIn<sub>5</sub>, where the magnetic moments lie on the basal plane [8].

For  $Ce_2MIn_8$ , Cd doping enhances the antiferromagnetic transition temperature  $T_N$  for M = Rh and induces a magnetically ordered phase over the spin-glass phase for M = Ir[26]. Experiments on the Cd-doped Ce<sub>2</sub>RhIn<sub>8</sub> under applied pressure revealed that the  $Ce^{3+}$  magnetic moments rotate gradually from  $45^{\circ}$  with the *c* axis towards the *ab* plane up to 0.6 GPa [27]. The ordered moment rotation is clearly a CEF effect due to the anisotropy of the CEF GS, and it is very important to investigate the role of dimensionality when the tetragonal CEF tunes the  $Ce^{3+}$  (J = 5/2) GS doublet  $(|\Gamma_6\rangle = |\pm 1/2\rangle \text{ or } |\Gamma_7^{\pm}\rangle = \sqrt{1 - \alpha^2} |\pm 5/2\rangle \pm \alpha |\mp 3/2\rangle,$  $\alpha \in [0, 1]$ ) [28]. The effects of both Cd doping and applied pressure on the M = Rh member of the Ce-218 series were studied in a recent CEF investigation, since the moment rotation is strong evidence that the CEF parameters of the system are changing [27]. Based on the neutron-diffraction studies, a detailed CEF study suggested that Cd acts as an electronic tuning agent, which induces changes in the local density of states of the Ce ions, lowering the energy of the CEF excited states and thus flattening the orbital distribution of the GS, favoring AFM order [9,27,29–31].

In this paper, we have investigated the evolution of the magnetic properties of  $Ce_2Rh_{1-x}Ir_xIn_{8-y}Cd_y$  ( $0 \le x \le 1, y = 0, 0.21$ ) to gain further insight into the role of simultaneous Ir and Cd doping in the Ce-218 family. We have performed neutron magnetic diffraction (NMD) experiments to determine the magnetic structure of pure and Cd-doped  $Ce_2Rh_{0.5}Ir_{0.5}In_8$  compounds. To further investigate the influence of Ir and Cd in the CEF levels and GS of the Ce-218 compounds, a mean-field model was used to analyze the magnetic-susceptibility data of  $Ce_2Rh_{1-x}Ir_xIn_{7.79}Cd_{0.21}$  (x = 0, 0.5, 1). It consists of the tetragonal CEF Hamiltonian of a  $Ce^{3+}$  ion and anisotropic

interactions between local moments, fulfilling the role of an effective RKKY interaction [9,29]. In particular, the moment's direction was used as an experimental constraint in the model (except for  $Ce_2IrIn_8$ ). From these results, we were able to trace a possible trend for the CEF evolution with the simultaneous Cd and Ir substitution in the Ce-218 series.

#### **II. EXPERIMENTAL DETAILS**

Single-crystalline samples of  $Ce_2Rh_{1-x}Ir_xIn_{7.79}Cd_{0.21}$ (x = 0, 0.25, 0.5, 0.75, 1) and Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> were grown by the indium-flux method [32,33]. The stoichiometry of the transition metals Rh and Ir was determined through energydispersive x-ray spectroscopy (EDS). The Cd concentration in Ce-218 materials was determined in previous works [26,34]. The Cd-to-In ratio was determined through prompt gamma neutron activation analysis at NG7 of the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), indicating that 13% of the nominal concentration of Cd in a given crystal actually incorporates into said crystal. The tetragonal P4/mmm crystal structure and the lattice parameters were determined by x-ray powder diffraction. For the y = 0 and y = 0.21 compounds, no significant change in the lattice parameters was found. The magnetization measurements were performed in a commercial superconducting quantum interference device (SQUID)-vibrating-sample magnetometer (VSM), and the specific-heat measurements were performed in commercial equipment, using a small mass calorimeter and a quasiadiabatic thermal relaxation technique. Through resistivity measurements using the four-contactpoints configuration, the samples were screened and found to be free of surface contamination by residual by residual flux. Several crystals (about seven per batch) were screened through specific-heat and resistivity measurements to construct horizontal error bars for the alloyed samples, related to the Ir-concentration inhomogeneity within a given batch. We verified a 5% deviation from nominal Ir concentration in each case (one standard deviation).

The NMD experiments were carried out on the BT-4 (Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub>) and BT-9 (Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub>) thermal triple-axis neutron spectrometers at the NCNR. Selected crystals previously screened with typical dimensions of  $4 \times$  $3 \times 1$  mm were aligned using the Laue method at the NCNR. The samples were cooled in an Institut Laue-Langevin (ILL) orange cryostat. The undoped sample was cooled in a <sup>3</sup>He bottom-loading cryostat with a base temperature of 0.3 K, while the Cd-doped sample was cooled in pumped He with a base temperature of 1.7 K. Neutrons with incident energy E = 14.7 and 35 meV (pure and Cd-doped, respectively) were selected using the (002) reflection of a pyrolytic graphite monochromator, and filters were used to avoid the higher harmonics. Horizontal collimators in the configurations of 60-42-42-100 (BT-4) and 40-47-40-80 (BT-9) full width at half maximum (FWHM) were employed. For our experimental conditions, no absorption corrections were employed. At the employed energies, the neutron penetration length is longer (about 2 mm) than the thickness of the samples, and the obtained rocking curves for different domains indeed showed no significant changes in the intensities.



FIG. 1. Magnetic specific-heat data divided by temperature as a function of temperature for the (a) pure and (b) Cd-doped (y = 0.21) compounds. (c) Data adapted from Ref. [34] presenting the evolution of  $T_N$  and  $T_{MAX}$  as a function of the Cd concentration for Ce<sub>2</sub>Rh<sub>0.5</sub>In<sub>8-y</sub>Cd<sub>y</sub>. The dashed curves are guides to the eyes. *x* evolution of  $T_N$  and the freezing temperature  $T_g$  for (d) pure and (e) Cd-doped samples, as a function of Ir concentration. (f) Sommerfeld coefficient  $\gamma$  roughly estimated from the data in (a) and (b), using an entropy-balance construction. Vertical error bars indicate one standard deviation.

#### **III. RESULTS AND DISCUSSION**

Figure 1 shows the magnetic specific heat per temperature  $(c_{\text{mag}}/T)$  as a function of temperature for several Ir concentrations, of the undoped [Fig. 1(a)] and Cd-doped [Fig. 1(b)]  $Ce_2Rh_{1-x}Ir_xIn_8$  compounds. We obtained  $c_{mag}$  by subtracting from the total specific heat  $(c_p)$  the lattice contribution  $(c_{latt})$ assumed to be identical to the specific heat of  $La_2RhIn_8$ .  $T_N$ is determined by a peak in  $c_{\text{mag}}$ . Moreover, the coherence temperature  $T_{MAX}$  is related to the maximum in electrical resistivity  $\rho(T)$ , obtained from peaks in the derivative of  $\rho(T)$ [34]. The evolution of the characteristic temperatures  $T_N$  and  $T_g$  for the studied compounds is presented in Figs. 1(d) and 1(e). Ir-rich compounds have a lower ordering temperature, indicating that Ir tends to suppress magnetic interactions, similar to the trend exhibited in the Ce-115 series [22]. When doping with a fixed Cd concentration of 2.6% in the Irsubstituted compounds, one can see the enhancement of  $T_N$ when compared with their undoped relatives. These results are in good agreement with previous work [18,26,34]. The presence of Cd in the system also suppresses the low-T superconducting states for the Ir-rich compounds, similar to the Ce-115 series [22,26]. One can clearly see in Fig. 1(c) that  $T_N$  is enhanced as a function of Cd doping for fixed Ir concentration (x = 0.5). An unusual increase in  $T_{MAX}$  can also be seen, which is not expected within the Doniach-type scenario adopted to interpret the evolution of  $T_N$  in the series [35]. The behavior of  $T_{MAX}$  is in agreement with previous reports on the pure Rh and Ir compounds (x = 0, 1) due to electronic tuning [26,27].

From the data in Figs. 1(a) and 1(b), the Sommerfeld coefficient  $\gamma$  was estimated using an entropy-balance construction in the vicinity of  $T_N$ ,  $S(T_N - \epsilon) = S(T_N + \epsilon)$ . The same procedure was used around  $T_g$  for the Ce<sub>2</sub>IrIn<sub>8</sub> compound. Figure 1(f) presents the Sommerfeld coefficient as a function of Ir concentration for two different Cd dopings. Increasing the amount of Ir in the system roughly tends to enhance the Sommerfeld coefficient overall, regardless of the presence of Cd, due to the increase in the hybridization with out-of-plane In atoms [36], in agreement with the scenario observed in the Ce-115 compounds [37,38].

Once the grown batches were characterized for their macroscopic and structural properties, single crystals of  $Ce_2Rh_{0.5}Ir_{0.5}In_8$  and  $Ce_2Rh_{0.5}Ir_{0.5}In_{7.79}Cd_{0.21}$  were selected and oriented to perform the NMD experiments.

The magnetic structures of the Ce<sub>2</sub>RhIn<sub>7.79</sub>Cd<sub>0.21</sub> and Ce<sub>2</sub>IrIn<sub>7,79</sub>Cd<sub>0,21</sub> compounds were determined in previous investigations, using x-ray and neutron scattering [26]. There were no changes in the magnetic propagation vector  $\mathbf{q} =$  $(\frac{1}{2}, \frac{1}{2}, 0)$  in either of the Cd-doped samples when compared with Ce<sub>2</sub>RhIn<sub>8</sub> [17]. A staggered moment of 0.9(2)  $\mu_B$  per Ce at 2.0 K, tilted  $47(5)^{\circ}$  from the *ab* plane, was found for Ce<sub>2</sub>RhIn<sub>7.79</sub>Cd<sub>0.21</sub>. For Ce<sub>2</sub>IrIn<sub>7.79</sub>Cd<sub>0.21</sub> a staggered moment of 0.4(5)  $\mu_B$  per Ce at 2.0 K tilted 21(5)° from the *ab* plane was observed [26]. The fact that the magnetic moments of this series are tilted off plane could be reminiscent of the cubic CeIn<sub>3</sub>, which presents  $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and consequently their moments align along the [111] crystallographic direction [39,40]. Since the Ce-218s are bilayered compounds, one could argue that their crystalline environment holds resemblances to their cubic relatives, and this may be reflected by their CEF properties and magnetic structure. In this paper, we report new neutron-diffraction data obtained from the Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub> compounds.

Magnetic reflections were observed below  $T_N = 2$  K and 4.3 K for the Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and Cd-doped samples, respectively. Their positions were reciprocal-lattice points forbidden for nuclear scattering and consistent with the same AFM structure as the previously investigated Ce-218 compounds, characterized by the propagation vector  $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$ . Since Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> presents a low-*T* SC state below  $T_c = 0.5$  K, we also investigated the (h, 0, 0), (0, 0, l), and (2, 0, l) directions, as well as the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  peak, to rule out a possible onset of incommensurability. Indeed, no intensity was found at those positions.

Figure 2(a) displays the temperature dependence of the integrated intensity of the  $(\frac{1}{2}, \frac{1}{2}, 1)$  magnetic Bragg reflection measured for Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub> by warming the samples in the temperature ranges between T = 0.3 K and T = 2.8 K for the former and T = 1.4 K and T = 4.8 K for the latter. The solid curves are a fit to the data using the expression  $I/I_0 = (1 - T/T_N)^{2\beta}$ , which yields  $I_0 = 750(30)$  counts/min,  $\beta = 0.35(5)$ ,  $T_N = 2.3(3)$  K for the pure compound. Data analysis of the Cd-doped sample considered a combination of two order-parameter expressions due to the presence of different grains. The parameters of the best fit were given by a 10% phase described by  $I_0 = 650(20)$  counts/min,  $\beta = 0.3(1)$ ,  $T_N = 4.4(2)$  K and  $I_0 = 550(30)$ 



FIG. 2. (a) Temperature dependence of the neutron integrated intensity (square of the sublattice magnetization) of the  $(\frac{1}{2}, \frac{1}{2}, 1)$  magnetic reflection measured for the pure and Cd-doped Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub>. The incident neutron beam energy was 14.7 and 35 meV, respectively. Error bars indicate one standard deviation. The solid curves are a fit to the data using the expression  $I/I_0 = (1 - T/T_N)^{2\beta}$ , in the case of the undoped sample, and the data from the Cd-doped sample were fit considering a combination of two order-parameter expressions due to the presence of different grains. (b)  $\theta$  scans (sample rotation) of the same reflection for both studied samples at 0.3 and 1.4 K, respectively. The solid curves are fits using Voigt functions, to extract the integrated intensity. Their FWHMs are 0.36(4)° for Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and 0.29(2)° for Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub>.

counts/min,  $\beta = 0.15(5)$ ,  $T_N = 4.1(2)$  K for the dominant 90% phase. These values of  $T_N$  are in agreement with specific-heat measurements considering the uncertainty in Ir concentration for each batch. The order parameters of these transitions show a more three-dimensional (3D) Heisenberg-like behavior, similar to that observed in the Ce-115s, for the undoped sample, while the Cd-doped sample presented a more 2D Ising-like behavior [41].

Once the magnetic propagation wave vector is determined, the magnetic-moment orientation of the Ce<sup>3+</sup> ion to the crystallographic *c* axis needs to be determined to fully solve the magnetic structure of the studied compounds. As exemplified in Fig. 2(b), the integrated intensities of the  $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, l)$ magnetic Bragg peaks were obtained using Voigt fits in the  $\theta$ scans. These magnetic peaks were first normalized using the nuclear Bragg peaks (00*l*) for l = 1, 2, 3, 4, and 7, (11*l*) for l = 1, 2, 3, 4, 5, and 6, and (22*l*) for l = 0, 1, and 2. In barn units, the cross section for magnetic scattering in a collinear



FIG. 3. *l* dependence [in reciprocal lattice units (r.l.u.)] of  $\sigma(Q)$  for the magnetic peaks  $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, l)$  measured with (a) the neutron energy of 14.7 meV at T = 0.3 K for Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub>, for reflections with  $h = \frac{1}{2}$  and  $h = \frac{3}{2}$ , and (b) the neutron energy of 35 meV at T = 1.4 K for the magnetic reflections with  $h = \frac{1}{2}$  of Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub>. The curves in each panel represent the best fit using the model discussed in the text, and the errors bars represent one standard deviation.

structure, using unpolarized neutrons, is given by [17,42-44]

$$I_{M}(Q) = \left(\frac{\gamma r_{0}}{2}\right)^{2} \langle \mu \rangle^{2} |f(Q)|^{2} \sum_{\xi,\nu} (\delta_{\xi,\nu} - \hat{Q}_{\xi} \hat{Q}_{\nu}) F_{\xi}^{*}(Q) F_{\nu}(Q),$$
(1)

where  $(\gamma r_0/2)^2 = 0.07265 \text{ b}/\mu_B^2$ ,  $\langle \mu \rangle$  is the effective magnetic moment of the Ce<sup>3+</sup> ion, f(Q) is the Ce<sup>3+</sup> magnetic form factor [45], and  $F_{\nu}(Q)$  is the  $\nu$ th Cartesian component of the magnetic structure factor per Ce-218. The symmetry of the Ce-218 structure leads the calculations to be made considering the average  $\langle 1 - (\hat{\mathbf{Q}} \cdot \hat{\mathbf{z}}_n)^2 \rangle$  over possible domains, and the result is given by [17]

$$I_M(Q) = \left(\frac{\gamma r_0}{2}\right)^2 \langle \mu \rangle^2 |f(Q)|^2 |F_M(Q)|^2 \langle 1 - (\hat{\mathbf{Q}} \cdot \hat{\mathbf{z}}_{\mathbf{n}})^2 \rangle, \quad (2)$$

where  $F_M(Q)$  is the magnetic form factor calculated for the two Ce<sup>3+</sup> ions of the unit cell along the *c* axis and  $\hat{\mathbf{z}}_n$  is the unit vector of the magnetic moment.

In this case, considering the magnetic moment with arbitrary orientation in relation to the *c* axis, there are 16 magnetic domains with tetragonal symmetry. Such symmetry does not allow the NMD technique to determine its direction within the *ab* plane [43,44], only the moment direction relative to the unique *c* axis. Taking into consideration all 16 domains equally populated, the average term of Eq. (2) can be written as [17]

$$\langle 1 - (\hat{\mathbf{Q}} \cdot \hat{\mathbf{z}}_{\mathbf{n}})^2 \rangle = 1 - \frac{\cos^2 \Omega \, \cos^2 \eta + 2 \, \sin^2 \Omega \, \sin^2 \eta}{2}.$$
 (3)

Here,  $\Omega$  is the angle of **Q** related to the orientation of the moment within the basal plane and  $\eta$  is the angle between the moment direction and the basal plane.

TABLE I. NMD parameters for Ce<sub>2</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>In<sub>8-y</sub>Cd<sub>y</sub>. The angle  $\eta$  is in degrees, and the staggered moment  $\langle \mu \rangle$  per Ce ion is in Bohr magneton units  $\mu_B$ .

x	у	$T_N$ (K)	$\eta$ (deg)	$\langle \mu  angle \left( \mu_B  ight)$
0	0	2.8(1) <sup>a</sup>	52(2) <sup>a</sup>	$0.55(6)^{a}$
0.5	0	2.3(3)	20(3)	0.2(1)
0	0.21	$4.8(1)^{b}$	45(3) <sup>b</sup>	$0.90(5)^{b}$
0.5	0.21	4.1(2)	0(3)	0.9(2)
1	0.21	3.8(1) <sup>b</sup>	21(5) <sup>b</sup>	0.4(5) <sup>b</sup>
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<sup>b</sup>Ref. [26].

Figure 3 shows the *l* dependence of the experimental  $(\frac{1}{2}, \frac{1}{2}, l)$  and  $(\frac{3}{2}, \frac{3}{2}, l)$  magnetic intensities for the undoped compound [Fig. 3(a)] and  $(\frac{1}{2}, \frac{1}{2}, l)$  for the Cd-doped sample [Fig. 3(b)], compared with the magnetic cross section  $\sigma(Q)$  in millibarns, calculated using the model discussed in Eqs. (1)–(3). The solid curve in each panel displays the best fit obtained for the magnetic-moment direction for the  $h = k = \frac{1}{2}$  reflections, while the dashed curve represents the analog fit for  $h = k = \frac{3}{2}$ .

The NMD results are summarized in Table I for the previously investigated Ce-218 samples [17,26], as well as the present results for both Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and the Cd-doped Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub> compounds. One can see that when comparing the magnetic structure of each Cd-doped sample with its pure relative, Cd tends to rotate the magnetic moments towards the *ab* plane and, due to the larger ordered moments  $\langle \mu \rangle$  and higher  $T_N$ , enhance magnetic states, following the trend observed for M = Rh Ce-218 compounds [27]. Surprisingly, Ir doping seems to have a similar effect on the moment's direction, in contrast to the Ce-115 series, in which Ir rotates the moments out of the *ab* plane [8]. As stated previously, Ir doping is rotating the moments towards the *ab* plane and also increasing the hybridization in this family, as can be seen by the reduction of the staggered moment in Ir-rich compounds in comparison to Ce<sub>2</sub>RhIn<sub>8</sub>, even in the presence of Cd.

These modifications in the magnetic structure of  $Ce_2Rh_{1-x}Ir_xIn_{8-y}Cd_y$  followed by drastic changes in the GS properties of the compounds should be associated with an evolution of the CEF effects along the series. This is clearly shown by the Ce<sup>3+</sup> moment direction change, which is only affected by CEF effects [28]. In an attempt to investigate such evolution and gain insights into the energy-level separation and orbital character of the CEF levels in these compounds [26,27], we have analyzed the high-temperature anisotropy of the magnetic susceptibility. We note that fits of macroscopic data are not unique and should be taken with caution. In order to improve the accuracy of the fits, we considered the direction of the ordered moments as an experimental constraint. To perform this analysis, we have used a mean-field model which has been previously applied to other Ce-based HF compounds [46-48] and to both Ce-218 and Ce-115 compounds [27,29,49]. This theoretical model is based upon the Hamiltonian [29]

$$\mathcal{H} = K_{\text{AFM}} \sum_{i,j} \mathbf{J}_{i} \cdot \mathbf{J}_{j} - \mu \cdot \mathbf{B} + B_{2}^{0}O_{2}^{0} + B_{4}^{0}O_{4}^{0} + B_{4}^{4}O_{4}^{4}, \quad (4)$$

TABLE II. CEF parameters and exchange interactions between nearest ( $K_{\text{nearest}}$ ) and next-nearest neighbors ( $K_{\text{NNN}}$ ) for Ce<sub>2</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>In<sub>8-y</sub>Cd<sub>y</sub> compounds. Here, the interaction terms already account for the number of neighbors z as in  $zK_{\text{AFM}}$ , and it was suppressed just for notation simplicity. The transition temperatures  $T^*$  stand for  $T_g$  for Ce<sub>2</sub>IrIn<sub>8</sub> and  $T_N$  for the remaining compounds. All quantities are in kelvins. Note that 1 meV = 11.605 K.

x	у	$T^*$	$B_2^0$	$B_4^0$	$B_4^4$	K <sub>nearest</sub>	K <sub>NNN</sub>
0.5	0	2.0(3)	-8.0	0.33	1.7	7.7	0.33
1	0	0.6(1)	-6.1	0.24	1.2	10	0.15
1 <sup>a</sup>	0 <sup>a</sup>	0.6 <sup>a</sup>	$-8.5^{a}$	0.37 <sup>a</sup>	1.8 <sup>a</sup>	8.8 <sup>a</sup>	0.48 <sup>a</sup>
0.5	0.21	4.3(2)	-6.4	0.28	1.4	6.2	0.12
1	0.21	3.8(1)	-6.2	0.26	1.3	6.9	0.34

<sup>a</sup>CEF speculation.

where the term  $K_{AFM} > 0$  represents the nearest-neighbor local spin interaction  $\mathbf{J}_{i,j}$ , which mimics the RKKY interaction, the second term accounts for the Zeeman effect, and the remaining terms are the  $B_n^m$  CEF parameters and  $O_n^m$  equivalent Stevens operators [50]. They connect the angular momentum operators to coordinate operators in spherical symmetry and account for the CEF effects. For instance, for Ce<sup>3+</sup> (J = 5/2), the operator  $O_2^0 = 3\hat{\mathbf{J}}_{z,i}^2 - \mathbf{J}(\mathbf{J} + 1)$  generally favors in-plane alignment for positive  $B_2^0$  or along the *c* axis for negative  $B_2^0$ . A standard mean-field approximation ( $\mathbf{J}_i \cdot \mathbf{J}_j \sim z\mathbf{J} \cdot \langle \mathbf{J} \rangle$ ), where *z* is the number of nearest neighbors, is employed, allowing the interaction term of the Hamiltonian to be simplified to  $zK_{AFM}\mathbf{J} \cdot \langle \mathbf{J} \rangle$ . We considered two isotropic interactions between nearest and next-nearest neighbors.

The crystal-field parameters presented in Table II generate CEF schemes in good agreement with the determined magnetic structure and the anisotropy of magnetic susceptibility for the investigated samples, as seen in Fig. 4. The resulting CEF schemes are presented in Table III and depicted in Fig. 5. The fits indicate that the compounds' CEF GS is composed of  $|\Gamma_7^-\rangle = \sqrt{1-\alpha^2}|\pm 5/2\rangle - \alpha |\mp 3/2\rangle$  ( $\alpha \in [0, 1]$ ) followed by the first excited doublet  $|\Gamma_7^+\rangle = \alpha |\pm 5/2\rangle + \sqrt{1-\alpha^2} |\mp 3/2\rangle$  and a  $|\Gamma_6\rangle = |\pm 1/2\rangle$  doublet.

As shown in Fig. 5, some general trends can be established from these results. As suggested before, Cd doping favors magnetic states through tuning of the electronic properties of the system, lowering the CEF levels and possibly increasing

TABLE III. CEF scheme for  $Ce_2Rh_{1-x}Ir_xIn_{8-y}Cd_y$ .  $\Delta^{(i)}$  stands for the CEF energy of the *i*th excited state (in meV). The  $\alpha$  parameter is the contribution to the CEF GS, as explained in the text.

<i>x</i>	у	$\Delta^{(1)}$	$\Delta^{(2)}$	α
0	0	7(1) <sup>a</sup>	23(1) <sup>a</sup>	$0.64(5)^{a}$
0.5	0	8(2)	25(2)	0.64(5)
1	0	6(3)	18(3)	0.61(5)
1 <sup>b</sup>	0 <sup>b</sup>	9(3) <sup>b</sup>	28(3) <sup>b</sup>	$0.66(5)^{b}$
0	0.21	$7(1)^{a}$	$22(1)^{a}$	$0.64(5)^{a}$
0.5	0.21	7(2)	21(2)	0.66(5)
1	0.21	6(3)	20(3)	0.64(5)

<sup>a</sup>Refs. [27,51].

<sup>b</sup>CEF speculation.



FIG. 4. Magnetic-susceptibility data obtained at ambient pressure in an applied field of 0.1 T parallel to the *c* axis (open symbols) and to the *ab* plane (closed symbols). The solid curves are the corresponding fits to a CEF mean-field model for (a) Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub>, (b) Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub>, (c) Ce<sub>2</sub>IrIn<sub>8</sub>, and (d) Ce<sub>2</sub>IrIn<sub>7.79</sub>Cd<sub>0.21</sub>. The dashed curves in (c) correspond to a speculated CEF scheme explained in the text. The  $\eta$  angles in the figures were used solely as a constraint in the CEF fit. Note that 1 emu/(mol Oe) =  $4\pi \times 10^{-6}$  m<sup>3</sup>/mol.

the planar contribution of the low-lying CEF wave functions. This decrease in the CEF overall splitting is directly related to the moment rotation through single-ion anisotropy [27]. From this viewpoint, it is reasonable to extrapolate the Ce-115 trend in which Cd-doped Ce-218 compounds would be unlikely to become superconducting, owing to a flatter orbital distribution in the GS and a moment rotation towards the *ab* plane.

When considering the effect of Ir in the Ce-218 compounds, it could be naively expected from its Ce-115 relatives that the Ir presence should rotate the magnetic moments towards the *c* axis, while increasing the Ising orbital contribution, enhancing the Kondo effect and consequently inducing SC [9,11–13,31]. However, we see that Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> has its ordered moments aligned 20° from the *ab* plane, lower than pure Ce<sub>2</sub>RhIn<sub>8</sub>. This is followed by a  $T_N$  suppression, appearance of a disordered phase, and induced SC with critical temperatures lower than its Ce-115 relatives. The best fit of experimental data for Ce<sub>2</sub>IrIn<sub>8</sub> samples presents a higher planar contribution to the GS wave function. Besides, as shown in Fig. 5, the CEF levels of Ce<sub>2</sub>IrIn<sub>8</sub> and Ce<sub>2</sub>IrIn<sub>7.79</sub>Cd<sub>0.21</sub> are found to be lower than expected from the other investigated



FIG. 5. Proposed CEF schemes for  $Ce_2Rh_{1-x}Ir_xIn_{8-y}Cd_y$  compounds, along with their magnetic structures. †Data extracted from Ref. [27]. For  $Ce_2IrIn_8$ , we display both the CEF scheme originated from fit and the scheme marked as \* that follows the trend discussed in the text.

compounds. The changes in the CEF caused by this doping, in contrast to the Ce-115 family, increase the  $|\pm 5/2\rangle$  contribution of the GS. This striking difference is interpreted, in the context of our model, as an effect of the absence of Kondo interactions. This effect is known to play a role at low temperatures for these materials, particularly the Ir-rich compounds. Some consequences would be a lower  $T_N$  than expected from interaction terms and masked energy splittings, on account of the broadening of the energy levels caused by hybridization. As such, the presented CEF schemes for Ir-substituted Ce<sub>2</sub>RhIn<sub>8-y</sub>Cd<sub>y</sub> should be taken cautiously. Nonetheless, the fits are still able to provide some valuable information about the CEF scheme, especially with the constraint of the known direction of the magnetic Ce<sup>3+</sup> moments.

As previously discussed, the presence of a spin-glass phase supplies us with very little information to use as physical constraints. Thus the fitting of our data for pure Ce<sub>2</sub>IrIn<sub>8</sub> imposes a great challenge. The obtained crystal-field splittings  $\Delta_1$  between the GS and the first excited state and  $\Delta_2$ between the first and second excited states do not follow the expected Ce-218 trend for Ir [namely, the increase of  $\Delta_1$  $(7 \text{ meV} \rightarrow 8 \text{ meV} \text{ and for } x = 1, 6 \text{ meV}) \text{ and } \Delta_2 (16 \text{ meV})$  $\rightarrow$  17 meV in contrast to 12 meV (x = 1)] as Ir concentration increases. Alternatively, if we assume a monotonic evolution to the CEF effects by considering that the broadening of CEF levels due to the Kondo effect could be masking the actual separation of levels as the observed lowering of states, we can tentatively extrapolate the aforementioned trend seen from the other compounds (Ce<sub>2</sub>RhIn<sub>8</sub>, Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub>, and the investigated Cd-doped compounds). The speculated CEF scheme (identified by \* in Fig. 5 and with footnotes in Tables II and III) presents higher excited states which suit the trend since the CEF levels are more energetic as the Ir concentration increases. The resulting curve corresponds to the dashed curve in Fig. 4(c). It would fit the high-temperature magnetic anisotropy nicely, while the deviation at lower temperatures such as 60 K could be derived from the complexity of the GS of this compound against the simplicity of our model. In fact, recent angle-resolved photoemission spectroscopy (ARPES) measurements on Ce<sub>2</sub>IrIn<sub>8</sub> have found the coherent temperature of the material to be approximately 40 K, evidencing the complexity of the interplay between different interactions at the corresponding range of temperatures [52,53].

In addition to the evolution of  $\gamma$  and  $\langle \mu \rangle$ , this evidence seems to indicate that Ir substitution increases hybridization dramatically. The CEF levels are broad enough that this can be seen as an effective lowering of levels which induces the spin rotation towards the *ab* plane. This is captured by our model only in extremely hybridized cases such as  $Ce_2IrIn_{8-\nu}Cd_{\nu}$ compounds. This broadening and consequent spin rotation leave a smaller out-of-plane contribution to the anisotropy. At first sight, by increasing hybridization, Ir substitution tends to induce SC. However, the higher dimensionality of the Ce-218s is reflected in their CEFs since the flatter orbital distribution tends to favor an AFM GS, competing with the SC state. This interplay may explain their lower  $T_c$ 's when compared with the Ce-115s, i.e.,  $Ce_2Rh_{0.5}Ir_{0.5}In_8$  has  $T_c = 0.5$  K, while CeRh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>5</sub> becomes superconducting at 0.8 K [4,18]. At the same time, the  $T_c$ 's of the Ce-218s are higher than the critical temperature of CeIn3 achieved only under applied pressure ( $T_c = 230$  mK at 2.46 GPa), which supports our proposition that the more tridimensional the compound, the more magnetic states are favored at the expense of superconductivity [53,54]. This effect in the presence of disorder in the AFM state may give rise to the spin-glass phase observed in  $Ce_2IrIn_8$  [18,19]. In other words, if the disorder in  $Ce_2IrIn_8$ were to be suppressed so that it is a perfect crystal, we would likely find a continuous evolution from the AFM in Ce<sub>2</sub>RhIn<sub>8</sub> to a possibly different AFM GS in Ce<sub>2</sub>IrIn<sub>8</sub>. Our findings reinforce the claim that both SC states in Ce-218 have a different nature, even if the microscopic origin of the Ir-rich SC remains unknown [18]. For Cd-doped Ce<sub>2</sub>IrIn<sub>8</sub>, the hybridization could be strong enough that the GS and first excited states form an effective quartet GS. This is characteristic of cubic CEF symmetry, as exemplified by CeIn<sub>3</sub>, whose CEF scheme consists of a  $\Gamma_7$  GS with an admixed  $\Gamma_8$  excited quartet, and moments align in the [111] direction and would ultimately drive the moment out of the *ab* plane in Ce<sub>2</sub>IrIn<sub>7.79</sub>Cd<sub>0.21</sub> [55]. Other evidence of a cubiclike CEF environment, as shown in Table II, is that the  $B_4$  CEF parameters are comparable to the tetragonal  $B_2^0$  term in this family.

Recent density functional theory plus dynamic mean-field theory calculations based upon ARPES and optical conductivity measurements on Ce2IrIn8 have found evidence of CEF transitions at the same order of magnitude as our fit [56]. The results also seem to indicate that for temperatures as low as 30 K, the CEF splitting features in the quasiparticle peak intensity merge and are not clearly distinguishable, which could lead to all the CEF levels contributing to the Fermi surface. That would support our claim that the lowering and broadening of CEF levels and thermal occupation could be responsible for a flattening of the orbital anisotropy and favoring of AFM states. To clarify which CEF scheme should describe the Ir-rich systems, additional experiments such as XAS and INS, which would be very challenging given the large absorption cross sections, are required to understand and validate the proposed scenarios.

## **IV. CONCLUSIONS**

We report the magnetic structure of pure and Cd-doped Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> single-crystalline samples. We found no changes in the propagation vector when compared with the previously investigated Ce<sub>2</sub>RhIn<sub>8</sub>, Ce<sub>2</sub>RhIn<sub>7.79</sub>Cd<sub>0.21</sub>, and Ce<sub>2</sub>IrIn<sub>7.79</sub>Cd<sub>0.21</sub>. Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>8</sub> and Ce<sub>2</sub>Rh<sub>0.5</sub>Ir<sub>0.5</sub>In<sub>7.79</sub>Cd<sub>0.21</sub> presented their moments ordered closer to the *ab* plane, with  $\eta = 20(3)^{\circ}$  and  $\eta = 0(3)^{\circ}$ , respectively. The studied samples present almost no change in the screening of ordered moments, and the moments are slightly less compensated when compared with the pure and Cd-doped Ce<sub>2</sub>RhIn<sub>8</sub> samples. These results show that both Ir and Cd tend to rotate the ordered moments toward the *ab* plane and favor antiferromagnetic ground states in the Ce-218 series.

Our results agree with the Cd electronic tuning scenario since the Cd-doped Rh-Ir alloys seem to follow this trend as well. Although Ir enhances hybridization in these compounds, favoring the appearance of superconductivity at ambient pressure, it also mixes the low-lying CEF states, increasing the planar orbital contribution and driving the system to an AFM ground state instead of a SC one. These competing effects in the more 3D structure of the Ce-218 compounds with a higher level of defects [57–59] may give rise to the disordered phases found in the Ir-rich side of the phase diagram and also provide an interesting point of view regarding the lower- $T_c$  superconductivity this family hosts when compared with the Ce-115 series.

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- A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, UK, 1993).
- [2] J. D. Thompson and Z. Fisk, J. Phys. Soc. Jpn. 81, 011002 (2012).
- [3] P. G. Pagliuso, C. Petrovic, R. Movshovich, D. Hall, M. F. Hundley, J. L. Sarrao, J. D. Thompson, and Z. Fisk, Phys. Rev. B 64, 100503(R) (2001).
- [4] M. Nicklas, V. A. Sidorov, H. A. Borges, P. G. Pagliuso, J. L. Sarrao, and J. D. Thompson, Phys. Rev. B 70, 020505(R) (2004).
- [5] Guo-qing Zheng, N. Yamaguchi, H. Kan, Y. Kitaoka, J. L. Sarrao, P. G. Pagliuso, N. O. Moreno, and J. D. Thompson, Phys. Rev. B 70, 014511 (2004).
- [6] S. Kawasaki, G. Q. Zheng, H. Kan, Y. Kitaoka, H. Shishido, and Y. Onuki, Phys. Rev. Lett. 94, 037007 (2005).
- [7] Y. Chen, W. B. Jiang, C. Y. Guo, F. Ronning, E. D. Bauer, Tuson Park, H. Q. Yuan, Z. Fisk, J. D. Thompson, and X. Lu, Phys. Rev. Lett. **114**, 146403 (2015).
- [8] A. Llobet, A. D. Christianson, W. Bao, J. S. Gardner, I. P. Swainson, J. W. Lynn, J.-M. Mignot, K. Prokes, P. G. Pagliuso, N. O. Moreno, J. L. Sarrao, J. D. Thompson, and A. H. Lacerda, Phys. Rev. Lett. 95, 217002 (2005).
- [9] A. D. Christianson, E. D. Bauer, J. M. Lawrence, P. S. Riseborough, N. O. Moreno, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, E. A. Goremychkin, F. R. Trouw, M. P. Hehlen, and R. J. McQueeney, Phys. Rev. B 70, 134505 (2004).
- [10] T. Takimoto, T. Hotta, T. Maehira, and K. Ueda, J. Phys.: Condens. Matter 14, L369 (2002).
- [11] P. G. Pagliuso, N. J. Curro, N. O. Moreno, M. F. Hundley, J. D. Thompson, J. L. Sarrao, and Z. Fisk, Physica B (Amsterdam, Neth.) **320**, 370 (2002).
- [12] T. Willers, Z. Hu, N. Hollmann, P. O. Korner, J. Gegner, T. Burnus, H. Fujiwara, A. Tanaka, D. Schmitz, H. H. Hsieh, H.-J. Lin, C. T. Chen, E. D. Bauer, J. L. Sarrao, E. Goremychkin, M. Koza, L. H. Tjeng, and A. Severing, Phys. Rev. B 81, 195114 (2010).
- [13] T. Willers, F. Strigari, Z. Hu, V. Sessi, N. B. Brookes, E. D. Bauer, J. L. Sarrao, J. D. Thompson, A. Tanaka, S. Steffen, L. H. Tjeng, and A. Severing, Proc. Natl. Acad. Sci. USA 112, 2384 (2015).
- [14] M. Nicklas, V. A. Sidorov, H. A. Borges, P. G. Pagliuso, C. Petrovic, Z. Fisk, J. L. Sarrao, and J. D. Thompson, Phys. Rev. B 67, 020506(R) (2003).

Brazil; Grants No. 2006/60440-0, No. 2009/09247-3, No. 2015/15665-3, No. 2017/10581-1, No. 2018/11364-7, No. 2018/26512-1, No. 2019/04196-3, and No. 2019/26247-9), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Brazil), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (Brazil). The staff at the BT-4 instrument are gratefully acknowledged for providing an outstanding scientific environment during these experiments. The authors also acknowledge the Center for Semiconducting Compounds and Nanotechnologies at UNICAMP for providing the equipment and technical support for the EDS experiments.

- [15] S. Raj, Y. Iida, S. Souma, T. Sato, T. Takahashi, H. Ding, S. Ohara, T. Hayakawa, G. F. Chen, I. Sakamoto, and H. Harima, Phys. Rev. B 71, 224516 (2005).
- [16] C. Adriano, F. Rodolakis, P. F. S. Rosa, F. Restrepo, M. A. Continentino, Z. Fisk. J. C. Campuzano, and P. G. Pagliuso, arXiv:1502.02544.
- [17] W. Bao, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, Z. Fisk, and J. W. Lyn, Phys. Rev. B 64, 020401(R) (2001).
- [18] E. N. Hering, H. A. Borges, S. M. Ramos, M. B. Fontes, E. Baggio-Saitovich, M. A. Continentino, E. M. Bittar, L. Mendonça Ferreira, R. Lora-Serrano, F. C. G. Gandra, C. Adriano, P. G. Pagliuso, N. O. Moreno, J. L. Sarrao, and J. D. Thompson, Phys. Rev. B 82, 184517 (2010).
- [19] G. D. Morris, R. H. Heffner, N. O. Moreno, P. G. Pagliuso, J. L. Sarrao, S. R. Dunsiger, G. J. Nieuwenhuys, D. E. MacLaughlin, and O. O. Bernal, Phys. Rev. B 69, 214415 (2004).
- [20] G. Chen, S. Ohara, M. Hedo, Y. Uwatoko K. Saito, M. Sorai, and I. Sakamoto, J. Phys. Soc. Jpn. 71, 2836 (2002).
- [21] H. Fukazawa, H. Taira, Y. Kohori, G. Chen, S. Ohara, and I. Sakamoto, Physica B (Amsterdam, Neth.) 359, 181 (2005).
- [22] L. D. Pham, T. Park, S. Maquilon, J. D. Thompson, and Z. Fisk, Phys. Rev. Lett. 97, 056404 (2006).
- [23] M. Nicklas, O. Stockert, T. Park, K. Habicht, K. Kiefer, L. D. Pham, J. D. Thompson, Z. Fisk, and F. Steglich, Phys. Rev. B 76, 052401 (2007).
- [24] Q. Y. Chen, F. Ronning, E. D. Bauer, C. H. P. Wen, Y. B. Huang, and D. L. Feng, Phys. Rev. B 100, 235148 (2019).
- [25] K. Beauvois, N. Qureshi, R. Tsunoda, Y. Hirose, R. Settai, D. Aoki, P. Rodiere, A. McCollam, and I. Sheikin, Phys. Rev. B 101, 195146 (2020).
- [26] C. Adriano, C. Giles, E. M. Bittar, L. N. Coelho, F. de Bergevin, C. Mazzoli, L. Paolasini, W. Ratcliff, R. Bindel, J. W. Lynn, Z. Fisk, and P. G. Pagliuso, Phys. Rev. B 81, 245115 (2010).
- [27] D. S. Christovam, C. Giles, L. Mendonça-Ferreira, J. Leão, W. Ratcliff, J. W. Lynn, S. Ramos, E. N. Hering, H. Hidaka, E. Baggio-Saitovich, Z. Fisk, P. G. Pagliuso, and C. Adriano, Phys. Rev. B 100, 165133 (2019).
- [28] L. Brewer, in Systematics and the Properties of the Lanthanides, edited by S. P. Sinha, NATO ASI Series (Series C: Mathematical and Physical Sciences) Vol. 109 (Springer, Dordrecht, 1983), pp. 17–69.
- [29] P. G. Pagliuso, D. J. Garcia, E. Miranda, E. Granado, R. Lora Serrano, C. Giles, J. G. S. Duque, R. R. Urbano, C. Rettori, J. D.

Thompson, M. F. Hundley, and J. L. Sarrao, J. Appl. Phys. 99, 08P703 (2006).

- [30] R. R. Urbano, B.-L. Young, N. J. Curro, J. D. Thompson, L. D. Pham, and Z. Fisk, Phys. Rev. Lett. 99, 146402 (2007).
- [31] K. Chen, F. Strigari, M. Sundermann, Z. Hu, Z. Fisk, E. D. Bauer, P. F. S. Rosa, J. L. Sarrao, J. D. Thompson, J. Herrero-Martin, E. Pellegrin, D. Betto, K. Kummer, A. Tanaka, S. Wirth, and A. Severing, Phys. Rev. B 97, 045134 (2018).
- [32] P. G. Pagliuso, J. D. Thompson, M. F. Hundley, J. L. Sarrao, and Z. Fisk, Phys. Rev. B 63, 054426 (2001).
- [33] Z. Fisk and J. P. Remeika, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier, Amsterdam, 1989), Vol. 12, p. 53.
- [34] C. Adriano, Ph.D. thesis, Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, 2009.
- [35] S. Doniach, in Valence Instabilities and Related Narrow Band Phenomena, edited by R. D. Parks (Plenum, New York, 1977), p. 169.
- [36] J. H. Shim, K. Haule, and G. Kotliar, Science 318, 1615 (2007).
- [37] H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Phys. Rev. Lett 84, 4986 (2000).
- [38] C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, and P. Monthoux, J. Phys.: Condens. Matter 13, 17 (2001).
- [39] A. Benoit, J. X. Boucherle, P. Convert, J. Flouquet, J. Palleau, and J. Schweizer, Solid State Commun. 34.5, 293 (1980).
- [40] Y. Kohori, T. Kohara, Y. Yamato, G. Tomka, and P. C. Riedi, Physica B (Amsterdam, Neth.) 281-282, 12 (2000).
- [41] W. Bao, G. Aeppli, J. W. Lynn, P. G. Pagliuso, J. L. Sarrao, M. F. Hundley, J. D. Thompson, and Z. Fisk, Phys. Rev. B 65, 100505(R) (2002).
- [42] J. W. Lynn, J. Appl. Phys. 75, 6806 (1994).
- [43] G. L. Squires, Introduction to the Theory of Thermal Neutron Scattering (Dover, Mineola, NY, 1996).
- [44] G. Shirane, S. M. Shapiro, and J. M. Tranquada, *Neutron Scattering with a Triple-Axis Spectrometer: Basic Techniques* (Cambridge University Press, Cambridge, UK, 2002).

- [45] M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1245 (1962).
- [46] C. Adriano, P. F. S. Rosa, C. B. R. Jesus, J. R. L. Mardegan, T. M. Garitezi, T. Grant, Z. Fisk, D. J. Garcia, A. P. Reyes, P. L. Kuhns, R. R. Urbano, C. Giles, and P. G. Pagliuso, Phys. Rev. B 90, 235120 (2014).
- [47] C. Adriano, P. F. S. Rosa, C. B. R. Jesus, T. Grant, Z. Fisk, D. J. Garcia, and P. G. Pagliuso, J. Appl. Phys. 117, 17C103 (2015).
- [48] P. F. S. Rosa, R. J. Bourg, C. B. R. Jesus, P. G. Pagliuso, and Z. Fisk, Phys. Rev. B 92, 134421 (2015).
- [49] R. Lora-Serrano, C. Giles, E. Granado, D. J. Garcia, E. Miranda, O. Agüero, L. Mendonça Ferreira, J. G. S. Duque, and P. G. Pagliuso, Phys. Rev. B 74, 214404 (2006).
- [50] K W H Stevens, Proc. Phys. Soc. A 65, 209 (1952).
- [51] A. Malinowski, M. F. Hundley, N. O. Moreno, P. G. Pagliuso, J. L. Sarrao, and J. D. Thompson, Phys. Rev. B 68, 184419 (2003).
- [52] H. Liu, Y. Xu, Y. Zhong, J. Guan, L. Kong, J. Ma, Y. Huang, Q. Chen, G. Chen, M. Shi, Y. Yang, and H. Ding, Chin. Phys. Lett. 36, 097101 (2019).
- [53] E. N. Hering, H. A. Borges, S. M. Ramos, M. B. Fontes, E. Baggio-Saitovich, E. M. Bittar, L. Mendonça-Ferreira, R. Lora-Serrano, C. Adriano, P. G. Pagliuso, J. L. Sarrao, and J. D. Thompson, Physica B (Amsterdam, Neth.) 403, 780 (2008).
- [54] S. Kawasaki, M. Yashima, Y. Kitaoka, K. Takeda, K. Shimizu, Y. Oishi, M. Takata, T. C. Kobayashi, H. Harima, S. Araki, H. Shishido, R. Settai, and Y. Onuki, Phys. Rev. B 77, 064508 (2008).
- [55] W. Knafo, S. Raymond, B. Fåk, G. Lapertot, P. C. Canfield, and J. Flouquet, J. Phys.: Condens. Matter 15, 3741 (2003).
- [56] B. G. Jang, B. Goh, J. N. Kim, H. Kang, J. H. Shim, H. Choi, K. Haule, and G. Kotliar, arXiv:2007.10641.
- [57] R. T. Macaluso, J. L. Sarrao, N. O. Moreno, P. G. Pagliuso, J. D. Thompson, Frank R. Fronczek, M. F. Hundley, A. Malinowski, and J. Y. Chan, Chem. Mater. 15, 1394 (2003).
- [58] E. G. Moshopoulou, Z. Fisk, J. L. Sarrao, and J. D. Thompson, J. Solid State Chem. 158, 25 (2001).
- [59] E. G. Moshopoulou, R. M. Ibberson, J. L. Sarrao, J. D. Thompson, and Z. Fisk, Acta Crystallogr., Sect. B: Struct. Sci. 62, 173 (2006).