First order ferromagnetic transition in binary $CeIn_2$

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Measurements of the magnetic, thermal, and transport properties of the $CeIn_2$ binary alloy are consistent with a paramagnetic-ferromagnetic transition at $T_C=22$ K. A discontinuity in the magnetic entropy, electrical resistivity and thermal expansion, and a huge anomaly in the specific heat of 113 J/mol K ($\Delta c_{mag}=103$ J/mol K), at the magnetic transition, are observed. In addition, the Arrott plots show negative slope at low fields, the field-cooling and field-warming magnetization present irreversibility, and both the susceptibility and the resistivity evidence a small thermal hysteresis of 0.05 K. Moreover, the values of the entropy change calculated from the magnetization data using the Clausius-Clapeyron equation are in good agreement with those directly obtained from the specific-heat data. The joint analysis of all these results provides evidence for the first order character of this magnetic transition in $CeIn_2$.

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I. INTRODUCTION

Magnetic phase transitions is a relevant topic in condensed-matter physics and material science research. The length and time scale of fluctuations diverge when approaching the transition temperature leading to singularities in many physical properties and a variety of rich phenomena.[1] The singularities in thermodynamic quantities depending on external parameters such as temperature, pressure, magnetic field, and chemical composition characterize these transitions.[2,3] In the last decade a new kind of phase transitions occurring at zero temperature without thermal fluctuations has given rise to considerable new insight.[4,5] These quantum phase transitions due to quantum fluctuations could be related to new states of matter, as observed, for instance, in the transition from a superfluid to a Mott insulator phase.[6] Although the archetypal example of continuous phase or second-order transitions is the magnetic ferro/antiferromagnetic to paramagnetic transition, there are several examples where a first order one (characterized by a latent heat and phase coexistence) is linked to remarkable properties such as the giant magnetocaloric effect,[7] and to the colossal magnetoresistance in manganites[8] and pyrochlores.[9]

Our study of strongly correlated Ce-based compounds such as the ferromagnetic Kondo lattice CePt (Ref. 10) and their chemical dilutions $CeNi_xPt_{1-x}$ (Ref. 11) and $CeNi_{1-x}Cu_x$ (Ref. 12), as well as with light and heavy rare earths, has allowed us to ascertain that although the interatomic distance has been used as a main parameter to associate with the appearance of the ferro or antiferromagnetic character of these compounds, the experimental results indicate that it is the electronic state, and, in particular, the density of states at the Fermi level and the Fermi surface shape, which are the driving parameter to the observed changes in the magnetic behavior in these systems.[13,14] Within the framework of these studies we have prepared the binary $CeIn_2$ alloy, which was found to be ferromagnetic below 22 K, one of the highest ferromagnetic ordering temperatures of these kinds of compounds. The experimental results for this sample presented here point toward a first order transition. The nature of this transition connecting the ferromagnetic and paramagnetic states merits special attention, and surely new physics could be revealed in further studies of this magnetic material. In fact, the first order character in Ce compounds has until now been associated with changes from antiferromagnetic to antiferro/ferromagnetic state, for instance, Ce_3Bi_4 intermetallic shows a first order transition from incommensurate magnetic phase at 4.4 K to noncollinear ferromagnetic phase at 3.3 K.[15] $CeRu_2Ge_2$ exhibits a double transition from a paramagnetic to an antiferromagnetic and then to a ferromagnetic state with $T_N \approx 8.3$ K and $T_C \approx 7.5$ K, respectively.[16] The sequence of second-order transition at $T_N \approx 35$ K and first order ones at $T_N \approx 25$ K was found for $CeRh_2Si_2$, as proved very recently by pressure experiments.[17] Indeed, the situation that this transition appears in a Ce compound provides an additional interest related to the interesting phenomena observed in strongly correlated electron materials, such as the existence of local inhomogeneities, phase coexistence, clusterization processes,[12] and the non-Fermi-liquid behavior.[18] In addition, the use of chemical and hydrostatic pressure would allow to study the evolution of T_C and the stability range of such first order transition, and when approaching to zero-temperature quantum critical point.

II. EXPERIMENTAL DETAILS

In the present work we have focused our attention on the first order nature of the magnetic transition in $CeIn_2$ revealed by measurements of magnetic, thermal, and transport properties, and additionally, by neutron diffraction experiments at different temperatures. The sample $CeIn_2$ was prepared by

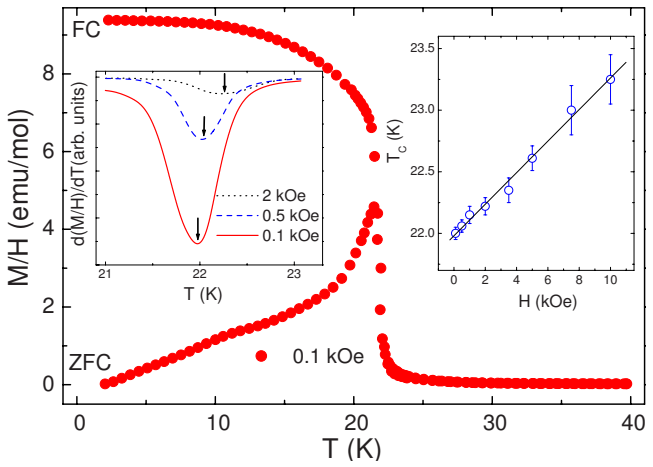

FIG. 1. (Color online) Temperature dependence of ZFC-FC curves at the magnetic field of 0.1 kOe. In the left inset, the minimum in the first derivative estimates the T_C. The right inset shows the field dependence of T_C. The shift of T_C to higher temperatures follows a nearly linear dependence, which is a characteristic of first order magnetic transitions.

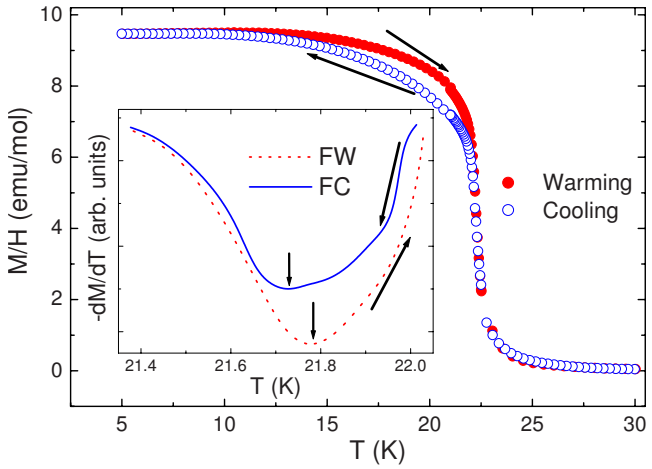

FIG. 2. (Color online) Temperature dependence of FW and FC magnetization curves at the magnetic field of 0.05 kOe. A large irreversibility in a wide temperature range between both curves is observed. In the inset, the first derivative of these curves around the transition shows a thermal hysteresis of 0.05 K, as observed from the shift of the temperature minimum.

arc melting of suitable amounts of the starting materials Ce(3N), In (5N) (all Johnson Matthey) in an arc furnace under Ar atmosphere. The analysis of x-ray diffraction patterns is consistent with the orthorhombic $CeCu_2$-type structure with unit-cell parameters a=4.742(1) Å, b=7.611(1) Å, and c=9.051(1) Å in agreement with what has been previously reported.[19]

Thermal, transport, and magnetic properties were collected in Quantum Design MPMS and PPMS devices in the temperature range 2–300 K and magnetic fields up to 90 kOe. Measurements of the magnetization as function of temperature were carried out in zero-field-cooling (ZFC), field-cooling (FC), and field-warming (FW) regimes. In the ZFC one, the magnetization was measured while warming up the sample after being cooled down from the paramagnetic state under no applied magnetic field. In the FC regime, the measurements were collected while cooling down the sample in an applied magnetic field and, finally, the FW curves were collected while warming up the sample in the presence of the same magnetic field than the one applied while cooling down the sample. Thermal expansion was measured using a miniature capacitance dilatometer.[20] Neutron diffraction experiments were carried out at the D20 two-axis diffractometer at the high-flux reactor of the Institute Laue-Langevin, Grenoble. It was necessary to extend the data-collection time for each spectrum (2, 15, and 25 K) up to 8 h because of the high neutron absorption of In element.

III. RESULTS AND DISCUSSION

The ferromagnetic order in $CeIn_2$ has been established, by measurements of ZFC and FC curves under an applied magnetic field of 0.1 kOe, as shown in Fig. 1. The saturation can be observed as the lower temperatures are approached, in the FC curve, as is expected for a ferromagnetic material. On the other hand, the ZFC curve reflects some degree of irreversibility, indicating the presence of a significant magnetocrystalline anisotropy and an interplay with exchange interactions while the thermal-energy changes. In the left inset, the minimum of the first derivative of the dc magnetic susceptibility (M/H) gives an estimate of the temperature of the ferromagnetic transition (T_C). This minimum shifts to higher temperatures when the magnetic field increases, and follows a nearly linear dependence, as shown in the right inset. This last feature is characteristic of first order magnetic transitions.[21,22] Another trademark of this kind of transitions is the existence of thermal hysteresis. In order to look for this hysteresis, measurements of the temperature dependence of the magnetization at the magnetic field of 0.05 kOe were carried out around T_C, with the smallest allowed step, in the FC and FW regimes, and the result is depicted in Fig. 2. A large irreversibility is observed in a relatively wide temperature range between both curves, as found in other materials with a first order transition.[23] In the inset, the first derivative of the warming and cooling curves shows a difference at the minimum (at the transition temperature) of 0.05 K, indicating the existence of a small thermal hysteresis and, therefore, pointing to a first order nature of the magnetic transition in $CeIn_2$. Another distinctive feature of the ferromagnetic behavior is the existence of hysteresis loops below the magnetic transition. In this sense, we present in Fig. 3 the hysteresis loop of $CeIn_2$ alloy at 6 K. In the inset, details of the low magnetic field region are depicted, and values for the remanence (M_r=0.74μ_B/mol) and coercivity (H_C =0.95 kOe) are indicated.

The ac magnetic susceptibility is a very convenient technique for the study of the magnetic behavior of materials with different magnetic phases and/or dynamic properties. In Fig. 4, the results of the ac magnetic susceptibility in $CeIn_2$ at the frequency of 1 kHz, for measurements on cooling down and warming up in temperature is presented. A peak appears in both the real and imaginary components near to 22 K, indicating a transition from paramagnetic to long-

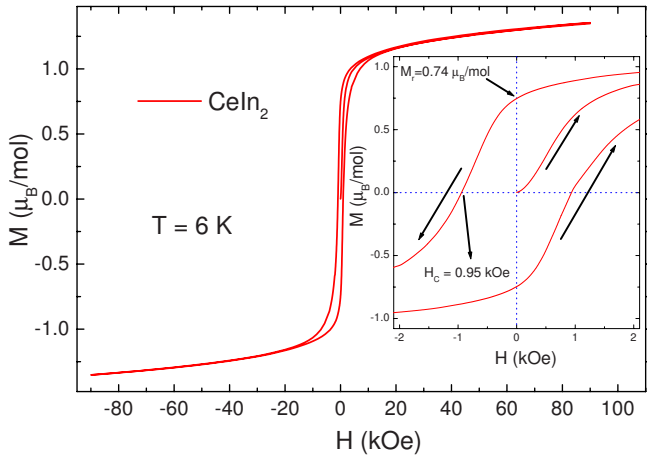

FIG. 3. (Color online) Hysteresis loop at 6 K for the $CeIn_2$ alloy. In the inset, details of the low magnetic field region with the values of remanence (M_r=0.74μ_B/mol) and coercivity (H_C=0.95 kOe) are depicted.

range magnetic ordering at this temperature. It is interesting to note that the curves obtained by warming and cooling do not coincide with each other for a wide temperature range, which is consistent with the results from dc magnetic susceptibility at 0.05 kOe (see Fig. 2), which can be ascribed to a first order nature of this magnetic transition. This hysteretic behavior of the ac susceptibility resembles the one reported in single and polycrystalline Tb and Dy, which is the result of the presence of metastables states influenced by the interplay of domain nucleation, domain-size changes, domain-wall pinning, and magnetocrystalline anisotropy with a dependence upon the thermal history.[24,25] In addition, the shift of 0.05 K of the maximum of the in-phase (χ') component, indicating a thermal hysteresis, as shown in the inset, is on the order of the one observed, for instance, in UO_2 (Ref. 26)

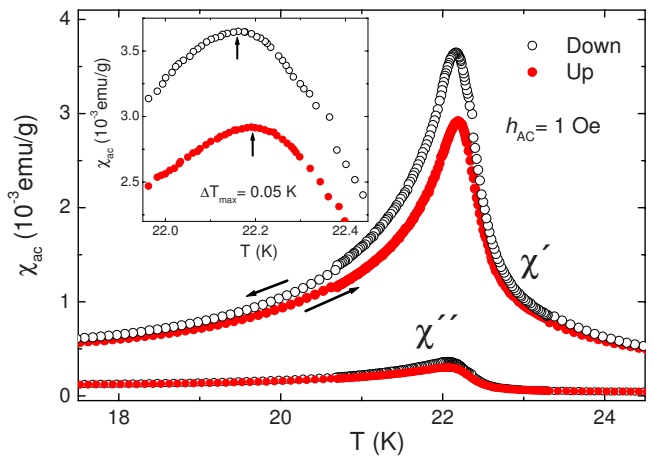

FIG. 4. (Color online) In-phase (χ') and out-phase (χ'') components of the ac magnetic susceptibility at the frequency of 1 kHz for the $CeIn_2$ compound. Measurements both on cooling down and warming up in temperature are presented. The inset details the temperature range around the maximum of χ' for both curves showing a small hysteresis of 0.05 K, as obtained from the positions of the maxima.

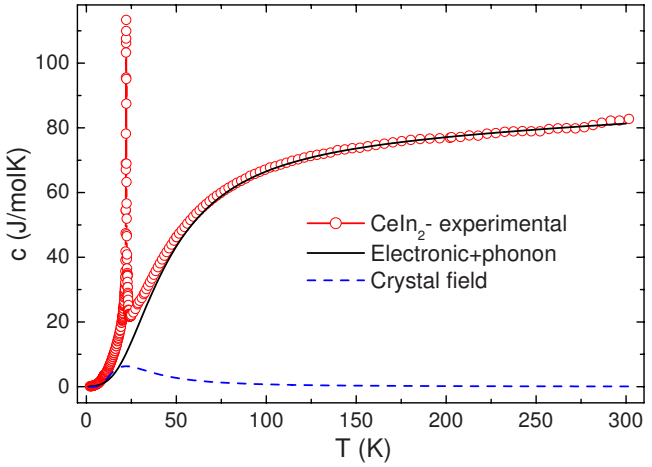

FIG. 5. (Color online) Temperature dependence of the specific heat of the $CeIn_2$ alloy. The estimate of the electronic+phonon and the crystal-field contributions (see text) are also shown. A huge peak of 113 J/mol K at 22 K is observed, which is the hallmark of a first order transition.

and $U_2Rh_3Si_5$,[27] both showing first order antiferromagnetic transitions at T_N=30 and 26 K, respectively. However, the structural disorder, always present in polycrystalline samples, may affect the thermal hysteresis around the transition.[28] In fact, the influence of disorder in polycrystalline samples might be so strong that it can even reverse the sense of the hysteresis.[29]

In Fig. 5, the temperature dependence of the specific heat in the temperature range between 2 and 300 K is presented. A huge peak of 113 J/mol K appears at 22 K, in good agreement with the temperature of the magnetic transition estimated from the ac (dc) magnetic susceptibility measurements. The magnitude of this peak is one order of magnitude larger than the value of 12.5 J/mol K expected for a second-order transition from mean-field theory for the Ce^{3+} ion, and provides evidence for the first order character of this transition. This first order nature can also be analyzed from the study of the magnetic entropy (S_{mag}), calculated as $S_{mag}=\int(c_{mag}/T)dT$, where c_{mag} is the magnetic contribution to the specific heat. For this purpose, we have determined c_{mag} from the analysis of the specific-heat data for $T>24$ K, which yields the values of γ=25(5) mJ/mol K^2 for the electronic coefficient and θ_D=185(5) K for the Debye temperature. During the fitting procedure, the crystal-field contribution with parameters Δ_1 and Δ_2 for the excited crystal-field levels, corresponding to the splitting of sixfold degenerate ground state of Ce^{3+} into three doublets in orthorhombic symmetry, was also considered. Details of these contributions are also depicted in Fig. 4. Thus, c_{mag} for the $CeIn_2$ alloy has been obtained by subtraction of the electronic and phonon contributions, and the result is shown in Fig. 6. Both the huge value of 103 J/mol K obtained for c_{mag} and the drop of S_{mag} at T_C are consistent with the first order character of the transition. Although this drop of S_{mag} at T_C is somehow smoothed, as expected from the polycrystalline nature of the sample,[28] it is clearly much steeper than that usually observed in second-order transitions.[16] A comparison between first and second-order transitions can be easily seen, for in-

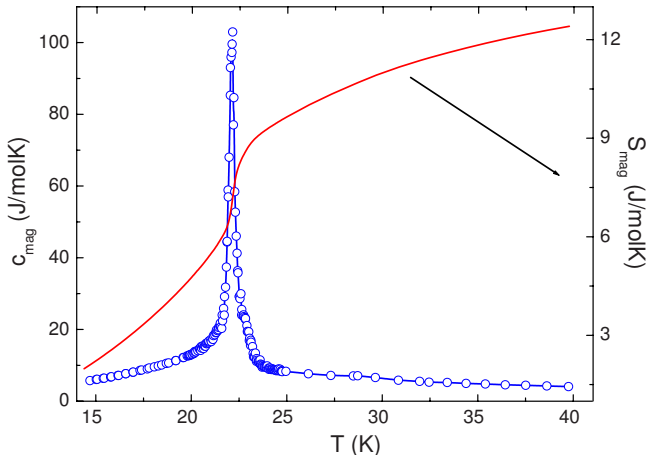

FIG. 6. (Color online) Temperature dependence of c_{mag} and S_{mag} for the $CeIn_2$ alloy. A huge peak of 103 J/mol K at 22 K is observed in c_{mag}, which is the hallmark of a first order transition. The magnetic entropy S_{mag} shows an abrupt variation at the transition, also consistent with this first order nature.

stance, in the study of chemically disordered manganites.[30] On the other hand, S_{mag} reaches a value close to R ln 6 at 300 K, as expected for the fully populated crystal-field levels, and is close to R ln 2 at T_C (see Fig. 6). This result indicates a magnetic order arising from a doublet ground state, as obtained from the analysis of specific-heat data above the magnetic transition, with the values of $\Delta_1=55$ K and $\Delta_2=65$ K for the excited doublets.

The field dependence of the specific heat is presented in Fig. 7. The peak associated to the magnetic transition broadens and shifts to higher temperatures when the magnetic field increases. This feature is consistent with ferromagnetic order. Under magnetic field, the variation in the isothermal entropy $[-\Delta S=S(H,T)-S(0,T)]$ reaches a maximum of 4.14 J/mol K (11 J kg^{-1} K^{-1}) at 23.5 K and 90 kOe. Thus, the magnetocaloric effect is significant when compared with that reported for rare-earth systems $ErCo_2$ (38 J kg^{-1} K^{-1}) at 35 K and 90 kOe,[7] considering the smaller moment for Ce^{3+} ion. The values of $-\Delta S$ can also be obtained from the magnetic analog of the Clausius-Clapeyron equation: $dT/dH=-\Delta M/\Delta S$, valid for first order transitions.[21] In this equation, $\Delta M=M(H,T)-M(0,T)$ and dT/dH accounts the field dependence of the ordering temperature. Using the results of dc magnetic susceptibility, $dT_C/dH=1.28\times10^{-4}$ kOe^{-1} for the $CeIn_2$ (see right inset of Fig. 1), and the ΔM values extracted from the field and temperature dependence of the magnetization, we can calculate the $-\Delta S$ values from this equation, which are shown in Fig. 8. In this figure, we can observe that they are in excellent agreement with those obtained from the specific-heat data, what further support the first order character of the magnetic transition in the $CeIn_2$ alloy.

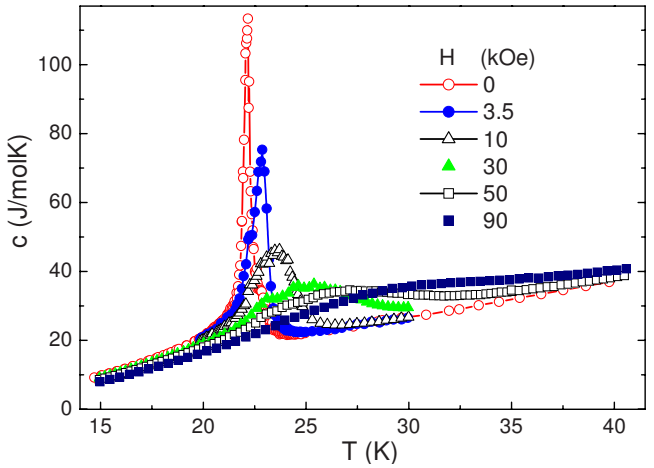

FIG. 7. (Color online) Temperature dependence of the specific heat for different magnetic fields. The shift of the peak to higher temperatures when the magnetic field increases is characteristic of ferromagnetic order.

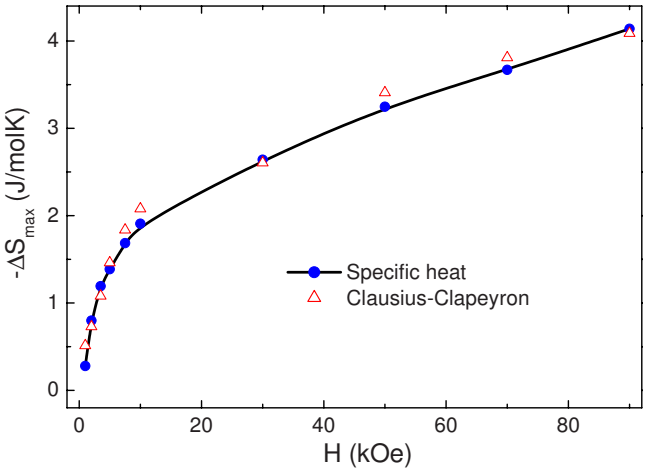

FIG. 8. (Color online) Values of the entropy change $-\Delta S$ obtained from the specific heat and from the Clausius-Clapeyron equation for different magnetic fields. Both set of values are in very good agreement.

The temperature dependence of the electrical resistivity of the $CeIn_2$ sample is presented in Fig. 9(a). At the ferromagnetic transition, a step decrease is clearly observed, which indicates the onset of magnetic correlations of the Ce^{3+} ions and a discontinuity at $T_C=22$ K associated to the first order nature of the magnetic transition. This is supported by the measurements performed on cooling and warming around the transition, as shown in the inset. These measurements exhibit a small thermal hysteresis of 0.05 K, better observed from the first derivatives presented in Fig. 9(b), as obtained from the shift of the maximum of the curves.

A similar behavior to that of the electrical resistivity is obtained for the thermal-expansion measurements, as presented in Fig. 10. The observed spontaneous magnetostriction of 3.6×10^{-5} suggests a moderate magnetoelastic coupling, which is similar to that reported for $U_2Rh_3Si_5$.[27]

A useful tool to discriminate between first and second order character of a magnetic transition is ascribed to Banerjee,[31] which is based on a similarity between the Landau-Lifshitz and Bean-Rodbell criteria. Using the expansion of thermodynamic potential in power series as a function of the order parameter, an expression for the inverse magnetic susceptibility $H/M=\alpha+\beta M^2$ can be obtained. A positive or negative slope (β) indicates a second or first order character of the magnetic transition, respectively. In Fig.

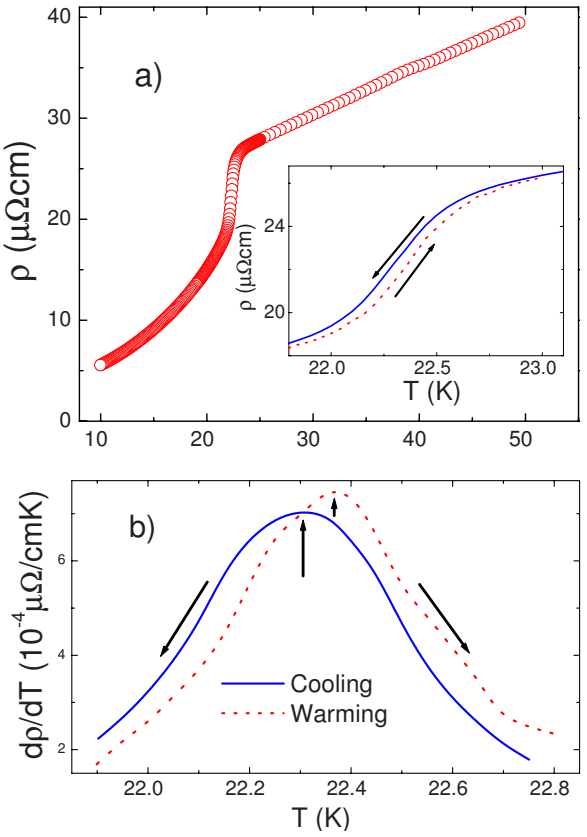

FIG. 9. (Color online) (a) Temperature dependence of the electrical resistivity of the $CeIn_2$ alloy The curve shows a step decrease at T_C=22 K, indicating a first order character of the magnetic transition. The inset shows the thermal hysteresis around the transition. (b) The difference between the positions of the maxima of the first derivative of the warming and cooling curves indicates a thermal hysteresis of 0.05 K.

11 several isotherm H/M vs M^2 plots for temperatures around the magnetic transition are presented. A negative slope can clearly be observed in the isotherm curves between 23 and 28 K, which, according to the criterion described above, is also an indication of the first order character of the magnetic transition.

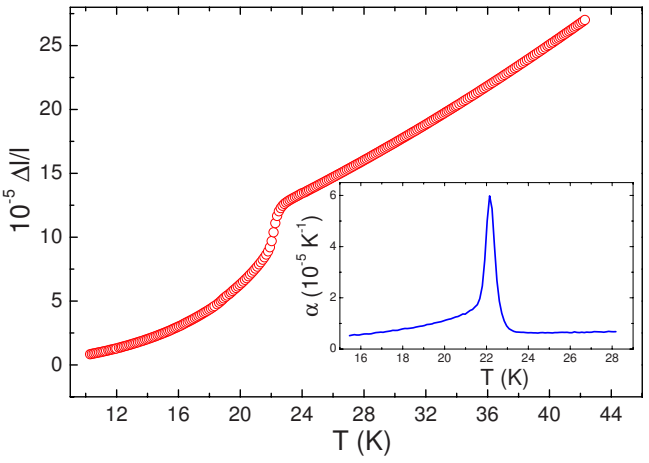

FIG. 10. (Color online) Temperature dependence of the thermal expansion with a step decrease at the transition. In the inset, the first derivative is shown.

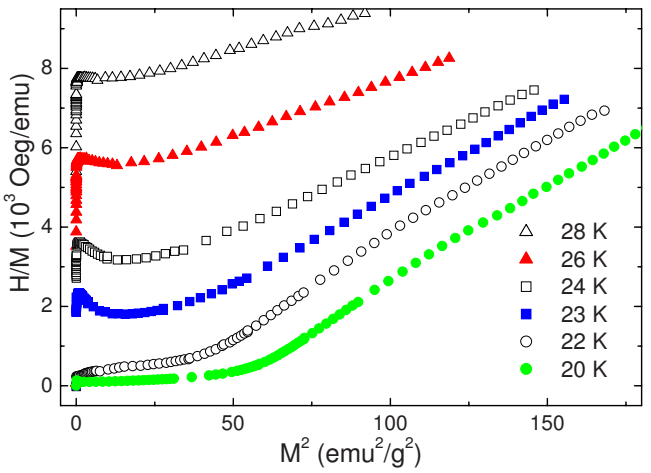

FIG. 11. (Color online) H/M vs M^2 isotherms around the magnetic transition. A negative slope at low fields, characteristic of first order phase transitions, is clearly observed at 23, 24, and 26 K.

In some cases, the first order transitions are induced by structural changes, as reported, for instance, in rare-earth systems such as RCo_2 with R=Er, Ho, and Dy.[7] In order to check for this possibility in $CeIn_2$, we have carried out neutron-diffraction experiments at different temperatures above and below the magnetic transition. From the resulting diffraction patterns, changes in the crystallographic structure were not observed. In addition, the results are consistent with a simple ferromagnetic structure with a propagation vector $\vec{k}=(0,0,0)$, a collinear arrangement of the magnetic moments along the a axis, and a magnetic moment for Ce^{3+} of $1.96(3)\mu_B$, as shown in Fig. 12.

First order transitions in some U, Np, and Pr compounds have been explained by the existence of multipole ordering associated to a particular crystal-field configuration; e.g., in

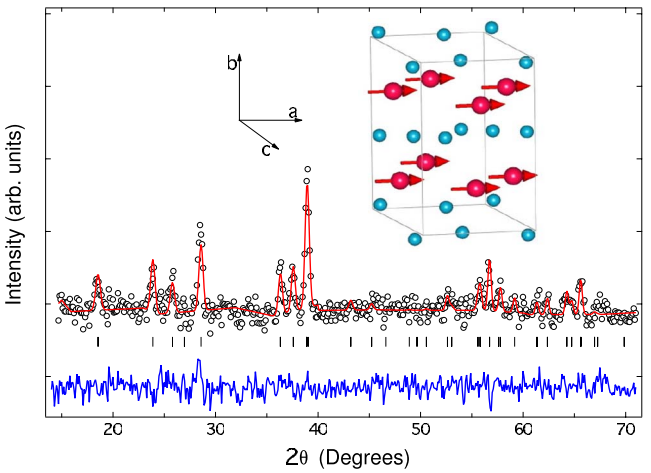

FIG. 12. (Color online) Magnetic contribution to the neutron diffraction patterns of $CeIn_2$ (2–25 K). Vertical marks correspond to the position of the allowed Bragg reflections for the magnetic phase. The solid lines are the calculated and the difference patterns. In the inset, details of the magnetic structure are depicted.

$U_2Rh_3Si_5$, the first order antiferromagnetic transition into a simultaneous spin quadrupolar ordering takes place around 26 K.[27] This possibility seems very unlikely in the case of $CeIn_2$, as it has an orthorhombic structure, then yielding a three-doublet crystal-field scheme.

IV. CONCLUSIONS

In conclusion, the results of measurements of thermal, transport, and magnetic properties for the $CeIn_2$ alloy have provided evidence for the existence of a first order ferromagnetic transition at T_C=22 K. This is supported by the discontinuity of the electrical resistivity, thermal expansion, and the magnetic entropy at T_C, a huge value of Δc_{mag} =103 J/mol K, a negative slope of the Arrott plots at low fields, the fact that the Clausius-Clapeyron equation is satisfied, and the existence of a small thermal hysteresis. Finally, it would be rewarding to carry out pressure experiments and study solid solutions of this alloy in order to reveal the influence of the disorder and chemical pressure effects on the magnetic transition, especially when T_C approaches zero temperature.

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