Kondo lattice and antiferromagnetic behavior in quaternary
\(\text{CeTAl}_4\text{Si}_2\) (\(T = \text{Rh, Ir}\)) single crystals

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Abstract

We report the synthesis and the magnetic properties of single crystalline CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$ and their non magnetic La-analogs. The single crystals of these quaternary compounds were grown using Al-Si binary eutectic as flux. The anisotropic magnetic properties of the cerium compounds were explored in detail by means of magnetic susceptibility, isothermal magnetization, electrical resistivity, magneto-resistivity and heat capacity measurements. Both CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$ undergo two antiferromagnetic transitions, first from the paramagnetic to an antiferromagnetic state at $T_{N1} = 12.6$ K and 15.5 K, followed by a second transition at lower temperatures $T_{N2} = 9.4$ K and 13.8 K, respectively. The paramagnetic susceptibility is highly anisotropic and its temperature dependence in the magnetically ordered state suggests the $c$-axis to be the relatively easy axis of magnetization. Concomitantly, isothermal magnetization at 2 K along the $c$-axis shows a sharp spin-flop transition accompanied by a sizeable hysteresis, while it varies nearly linearly with field along the [100] direction up to the highest field 14 T, of our measurement. The electrical resistivity provides evidence of the Kondo interaction in both compounds, inferred from its $-\ln T$ behavior in the paramagnetic region. The heat capacity data confirm the bulk nature of the two magnetic transitions in each compound, and further confirm the presence of Kondo interaction by a reduced value of the entropy associated with the magnetic ordering. From the heat capacity data below 1 K, the coefficient of the linear term in the electronic heat capacity, $\gamma$, is inferred to be 195.6 and 49.4 mJ/mol K$^2$ in CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$, respectively classifying these materials as moderate heavy fermion compounds. The main features of the magneto-resistivity measured at a particular temperature correlate nicely with the isothermal magnetization at the same temperature, nevertheless the data also suggest differences in the Fermi surface topology in the these two isostructural compounds. We have also carried out an analysis of the magnetization based on the point charge crystal electric field model and derived the crystal electric field energy levels which reproduce fairly well the peak seen in the Schottky heat capacity in the paramagnetic region.

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I. INTRODUCTION

Recently, we have reported the synthesis and magnetic properties of quaternary EuTAl$_4$Si$_2$ (T = Rh and Ir) single crystals, using the Al-Si binary eutectic as flux$^{1,2}$. The two Eu compounds initially order into an incommensurate amplitude modulated antiferromagnetic state at $T_{N1} = 11.7$ and $14.7$ K respectively, followed by a second transition to an equal moment, commensurate state at lower temperature $T_{N2}$. Though these two compounds prima-facie are antiferromagnetic, the isothermal magnetization curves at low temperatures (below $T_{N2}$) show a hysteresis right near the origin with a remnance; unlike any other antiferromagnetic material. The EuTAl$_4$Si$_2$ compounds adopt an ordered derivative of the ternary KCu$_4$S$_3$-type tetragonal, $tP8$, $P4/mmm$ structure, which leads to quaternary and truly stoichiometric 1:1:4:2 compounds, with a local fourfold axial ($4/mmm$) symmetry at the Eu site. These are a new addition to several quaternary rare earth-based compounds already known in the literature with 1:1:4:2 stoichiometry, which have been grown using aluminum as flux; for example, RNiAl$_4$(Ni$_x$Si$_{2-x}$), EuNiAl$_4$Si$_2$, RNiAl$_4$Ge$_2$, RAuAl$_4$Ge$_2$ and RAuAl$_4$(Au$_x$Ge$_{1-x}$)$_2$ where R is a rare earth metal$^{3,4}$. While most of the these compounds adopt the rhombohedral YNiAl$_4$Ge$_2$-type structure$^5$, the phases RAuAl$_4$(Au$_x$Ge$_{1-x}$)$_2$ and EuAu$_{1.95}$Al$_4$Ge$_{1.05}$ crystallize in the KCu$_4$S$_3$-type structure$^5$. Both structure types are characterized by the slabs of “AuAl$_4$X$_2$ (X = Si or Ge)” or “AuAl$_4$(Au$_x$Ge$_{1-x}$)$_2$” stacked along the c-axis with layers of R atoms in between. The Ce atoms in both CeAuAl$_4$Ge$_2$ and CeAuAl$_4$(Au$_x$Ge$_{1-x}$)$_2$ (x = 0.4) have been reported to be in a valence fluctuating state$^3$. This suggests the possibility of strong hybridization between the Ce-4$f$-orbitals and the itinerant electrons in these structure-types, which is known to lead to a variety of anomalous ground states, such as Kondo lattices, heavy fermions with huge effective electron masses, magnetically ordered states with reduced saturation moments$^6,7$. The Néel temperature in some heavy fermion, antiferromagnetic Kondo lattices can be tuned to zero using pressure as an external parameter, which leads to a quantum phase transition where the Fermi-Landau description of quasiparticles breaks down$^8$. It was therefore of interest to explore the formation of other RTAl$_4$Si$_2$ (T = Rh and Ir) compounds, in particular for R = Ce. We have been able to grow the single crystals for R = Ce and Pr and in this report we give a detailed description of properties of two Ce compounds. We find that both CeTAl$_4$Si$_2$ (T = Rh and Ir) compounds are dense Kondo lattice antiferromagnets, each undergoing two magnetic
transitions like the Eu-analogs.

II. EXPERIMENT

The single crystals of CeTAl$_4$Si$_2$ were grown by following the same experimental protocol as described in Ref. 1 for the Eu-compounds. Their Laue patterns were recorded using a Huber Laue diffractometer, while the phase purity was inferred from the powder x-ray diffraction pattern collected using a PANalytical x-ray diffractometer. The stoichiometry was checked by semiquantitative analysis performed by energy dispersive analysis by x-rays (EDAX). Well oriented crystals were cut appropriately by an electric discharge cutting machine for direction dependent measurements. The magnetization data were measured in a Quantum Design Superconducting Quantum Interference Device (SQUID) and Vibration Sample Magnetometer (VSM) magnetometers in the temperature range 1.8 to 300 K and fields up to 14 T. The electrical resistivity, magnetoresistivity and the heat capacity were measured in a Quantum Design Physical Properties Measurement System (PPMS). Heat capacity measurements down to 100 mK were performed using the dilution insert of QD-PPMS. A piston-cylinder type pressure cell was used to measure the resistivity of CeIrAl$_4$Si$_2$ at 23 kbar with Daphne oil as hydrostatic medium.

III. RESULTS

A. Structure

The compositions obtained from EDAX analysis confirmed the stoichiometric ratio of 1:1:4:2 to within 1 at.% for each element. The powder x-ray diffraction pattern of CeTAl$_4$Si$_2$ (T = Rh and Ir) are similar to those of Eu-analogs, and no extra peaks due to any parasitic phases were found. A Rietveld refinement using FullProf software based on the EuIrAl$_4$Si$_2$-type tetragonal crystal structure was performed. The obtained lattice parameters $a$ and $c$ are listed in Table I. It may be noted that similar to Eu compound, the lattice parameter $a$ is larger but $c$ is slightly shorter in Ir analog compared to that of Rh analog but overall the unit cell volume of CeIrAl$_4$Si$_2$ is slightly larger than that of the Rh-analog, which is in accordance with the larger atomic volume of Ir.
TABLE I: Lattice constants \( a \) and \( c \), and unit cell volume \( V \) of CeRhAl\(_4\)Si\(_2\) and CeIrAl\(_4\)Si\(_2\) as determined from the x-ray powder diffraction pattern.

|                | \( a \) (Å) | \( c \) (Å) | \( V \) (Å\(^3\)) |
|----------------|-------------|-------------|---------------------|
| CeRhAl\(_4\)Si\(_2\) | 4.223(2)   | 8.048(2)   | 143.54(2)           |
| CeIrAl\(_4\)Si\(_2\) | 4.236(3)   | 8.043(2)   | 144.34(2)           |

B. Magnetic susceptibility and magnetization

The magnetic susceptibility, \( \chi(T) \), of CeRhAl\(_4\)Si\(_2\) and CeIrAl\(_4\)Si\(_2\) below 300 K is shown in the main panel of Figs. 1(a) and 1(b), for field (0.3 T) applied along the [100] and [001] directions, respectively. The inverse susceptibility in the temperature range 1.8 to 300 K is plotted in the insets of Fig. 1(a) and (b). The susceptibility is highly anisotropic in the paramagnetic region in both compounds and a fit of the Curie-Weiss law, \( \chi = C/T - \theta_p \), to the high temperature data (100-300 K), represented by the solid lines, furnishes the Curie-Weiss parameters which are listed in Table II. The effective moments are close to the Ce\(^{3+}\)-free ion moment value of 2.54 \( \mu_B/\text{Ce} \). The highly anisotropic nature of the susceptibility is clearly reflected by the respective values of paramagnetic Curie temperature \( \theta_p \) which are more than one order of magnitude larger for \( H \parallel [100] \) in both compounds. In conformity with the trivalent nature of the Ce ions, the compounds order antiferromagnetically at \( T_{N1} = 12.6 \) and 15.5 K, and \( T_{N2} = 9.4 \) and 13.8 K in Rh and Ir compound, respectively. It may be noted that the absolute value of the polycrystalline averaged \( \theta_p \) (−101 and −92 K) is substantially higher than \( T_{N1} \). We believe it to be primarily due to the crystal electric field and anisotropic Kondo interaction (\textit{vide infra}) which contributes negatively to \( \theta_p \). In the simplest collinear two-sublattice antiferromagnet, the \( \chi \perp \) along the hard direction is temperature independent below \( T_N \) while \( \chi \parallel \) gradually decreases to zero as \( T \to 0 \). A weak temperature dependence of \( \chi \) along [100] in the two compounds indicates a hard \( ab \)-plane.

The magnetic field dependence of susceptibility \( (M/H) \) below \( T_{N1} \) was investigated at a few fields and the data are plotted in Figs. 1(c-f). The \( T_N \) decreases as the applied field is increased, as commonly observed in antiferromagnets. However, the decrease is more substantial for \( H \parallel [001] \) which is relatively the easy axis of magnetization. The
FIG. 1: (Color online) Magnetic susceptibility and inverse susceptibility (in inset) up to 300 K of (a) CeRhAl$_4$Si$_2$ and (b) CeIrAl$_4$Si$_2$. The dependence of $M/H$ on field is shown in (c-f) for $H \parallel [100]$ and $H \parallel [001]$, respectively. In (e) and (f) single color plots show ZFC (zero field cooled), FCC (field cooled cooling) and FCH (field cooled heating) data revealing field induced first order nature of transition at $T_{N2}$.

magnetization in both compounds at $T_{N2}$ exhibits hysteresis, which is more clearly discernible at $\sim 4$ T in CeRhAl$_4$Si$_2$ and at $\sim 6$ T in CeIrAl$_4$Si$_2$, thereby indicating that the transition at $T_{N2}$ has a first order character. The hysteresis is weaker at lower fields and it increases with increment in magnetic field till spin flop field.

The isothermal magnetization at 2 K is linear up to 14 T along [100] while there is a sharp spin-flop (metamagnetic-like) jump in the magnetization along the [001]-direction at
TABLE II: Effective moment and paramagnetic Curie temperature in CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$ along the principal crystallographic directions.

|                | CeRhAl$_4$Si$_2$ | CeIrAl$_4$Si$_2$ |
|----------------|------------------|------------------|
| $\mu_{\text{eff}}$ ($\mu_B$/f.u.) | $\theta_p$ (K)   | $\mu_{\text{eff}}$ ($\mu_B$/f.u.) | $\theta_p$ (K)   |
| $H \parallel [100]$ | 2.65            | $-155$          | 2.62            | $-140$          |
| $H \parallel [001]$ | 2.35            | 7.1             | 2.43            | 4               |

FIG. 2: (Color online) Isothermal magnetization curves at selected temperatures for (a) CeRhAl$_4$Si$_2$ and (b) CeIrAl$_4$Si$_2$ along [001] direction. The insets show the data at 2 K for $H \parallel [001]$ and $H \parallel [100]$. (c) and (d) show the data at selected temperatures for $H \parallel [100]$. The inset in (d) reveals two weakly first order changes which are also seen in the magnetoresistance data. (see Fig. 6).

5.3(6.4) T for CeRh(Ir)Al$_4$Si$_2$ (see Figs. 2 (a) and 2 (b)). The former behavior is typical of an antiferromagnet when the moments are perpendicular to the field. The field dependence thus clearly marks the easy and the hard-axes of magnetization. However, the magnetization is not zero along the easy-axis from the origin up to the spin-flop transition, indicating that the actual magnetic structure may deviate from the simple collinear two sub-lattice.
FIG. 3: (Color online) Electrical resistivity of (a) CeRhAl$_4$Si$_2$ and LaRhAl$_4$Si$_2$; (b) CeIrAl$_4$Si$_2$ and LaIrAl$_4$Si$_2$ along the major crystallographic directions. $\rho_{4f}$ is represented by solid lines. (c) and (d) show the low temperature data. $\rho_{4f}(T)$ data plotted on logarithmic temperature scale are shown in (e) and (f). Inset in (f) show the effect of pressure on $\rho(T)$ in CeIrAl$_4$Si$_2$ sample for $J \parallel [100]$. Microscopic technique of neutron diffraction is needed for the determination of exact magnetic structure of the ground state. It attains a value of 0.95 and 1.14 $\mu_B$/Ce at 14 T in CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$ respectively, which is lower than the saturation moment of Ce$^{3+}$ (2.14 $\mu_B$/Ce). We attribute the lower value to the combined effects of crystal electric field and partial quenching of the Ce moments due to Kondo screening.

One can observe a clear hysteresis in the vicinity of spin-flop transition. The hysteretic
behavior is also observed in the temperature dependence of magnetic susceptibility (mentioned above) and electrical resistivity (vide infra), revealing the presence of first order field induced effect. The spin-flop field value and the magnetization decrease with the increase of temperature. The magnetization for $H \parallel [100]$ is relatively insensitive to the variation in temperature as inferred from Figs. 2(c) and 2(d). The inset in Fig. 2(d) reveals two weakly hysteretic regions in the magnetization of CeIrAl$_4$Si$_2$ at 8 K.

C. Electrical Resistivity

Figs. 3(a-f) show the zero-field electrical resistivity $\rho(T)$ data of CeRhAl$_4$Si$_2$ (left panels) and CeIrAl$_4$Si$_2$ (right panels) for the current density parallel to [001] and [100] directions, respectively. The corresponding data for the non-magnetic La-reference compounds are also plotted. While anomalies at $T_{N1}$ and $T_{N2}$ for $J \parallel [001]$ are visible either in the $\rho$ vs $T$ or $d\rho/dT$ vs $T$ plots (not shown), the $\rho$ for $J \parallel [100]$ shows a sudden change of slope only at $T_{N2}$.

There is a considerable anisotropy in the resistivity, $\rho$ along [001] being larger compared to [100] in the entire temperature range. The residual resistivity ratio $\rho_{300K}/\rho_{2K}$ is 17.8 and 29.9 for $J \parallel [100]$ and [001], respectively for CeIrAl$_4$Si$_2$, compared to its corresponding values of 3.2 and 3.4 in CeRhAl$_4$Si$_2$. Additionally, while $\rho_{[001]}$ decreases as the temperature is decreased below 300 K, $\rho_{[100]}$ shows a slight negative temperature coefficient above 100 K. The 4$f$-derived part of the resistivity $\rho_{4f}$ is calculated by subtracting the $\rho(T)$ data of La-analog from the corresponding Ce-compound, which is also shown in Fig. 3(a) and 3(b) and replotted in 3(e) and 3(f) on a semi-logarithmic scale. $\rho_{4f}$ reveals a negative logarithmic slope along both directions which is a hallmark of the Kondo interaction. The high temperature peak in $\rho_{4f}$ in range 100-200 K, which arises due to interplay of Kondo interaction and crystal electric field levels, occurs at different temperatures along the two directions. The resistivity data thus reveal that these two Ce-compounds are dense anisotropic Kondo lattice antiferromagnets.

Preliminary resistivity data measured under an external applied pressure of 23 kbar in CeIrAl$_4$Si$_2$ is qualitatively in consonance with the Doniach phase diagram of a magnetic Kondo lattice. The data at ambient pressure and 23 kbar are shown in Fig. 3(e). It is observed that $T_{N2}$, indicated by an arrow in the Figure, decreases from 13 K at ambient
D. Magnetoresistance

The variation of resistivity with magnetic field at low temperatures is shown in Figs. 4(a-d). For $H$ applied along [100] and $J \parallel [001]$ the resistivity plots are qualitatively similar except that there is a gradual downward shift of $T_N$ with increasing field. On the other hand prominent changes are seen for $H \parallel [001]$ and $J \parallel [100]$. $T_N$ is suppressed relatively faster with a substantial hysteresis in the field-range where spin-flop occurs, revealing first order effects in conformity with the magnetization data. One also observes a slight upward kink at around 13 K in 5 T which persists at least up to 6.5 T in CeIrAl$_4$Si$_2$. This may be due to field induced superzone gap. The inset of Fig. 4(d) shows the hysteresis in the resistivity (on right scale) and $M(T)/H$ (on left scale) data at 6 T field applied parallel to [001]. There is a good agreement between the two measurements.

Magetoresistivity $MR$ was also probed by varying the field from zero to 14 T at selected pressure to 7 K at 23 kbar.
FIG. 5: (Color online) Magnetoresistance (MR) data of CeRhAl₄Si₂ (left panels) and CeIrAl₄Si₂ (right panels). (a) and (b) show the current and field-direction dependence of MR at 2 K up to 14 T. (c) and (d) demonstrate the close correspondence between isothermal magnetization and magnetoresistance data at 2 K.

temperatures, with the field and current density in various orientations and the results are plotted in Figs. 5 and 6. The magnetoresistance, $MR$ is defined as $MR = [\rho(H) - \rho(0)]/\rho(0)$. With reference to Fig. 5(a) the MR of CeRhAl₄Si₂ at 2 K for field applied in the ab-hard plane is small and attains a value of $\sim 3\%$ at 14 T. On the other hand for field applied along the easy-axis [001] the MR at its maximum is an order of magnitude larger. Initially the positive $MR$ increases with field, as expected in an antiferromagnet, jumps sharply at the spin-flop attaining a maximum of 30% and decreases sharply at higher fields and becomes negative as the magnetization gradually approaches saturation by field-induced parallel alignment of the Ce-magnetic moments. In the return cycle the $MR$ shows hysteresis in the spin-flop region, which corresponds nicely with the hysteresis in the magnetization as shown in Fig. 5(c).

For CeIrAl₄Si₂ the $MR$ for $H \parallel [001]$ is qualitatively similar (Figs. 5(b) and 5(d)) at low fields except that the $MR$ in the spin-flop region is even larger and exceeds 100%. Above
FIG. 6: (Color online) Temperature dependence of $MR(H)$ in CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$. The data in (c) and (e) are looking scattered due to the relatively smaller values of the $MR$.

The spin-flop the $MR$ drops sharply but unlike CeRhAl$_4$Si$_2$ it does not attain negative values but remains positive up to the highest field of 14 T. For field applied in the $ab$-hard plane viz. $J$ || [100] and $H$ || [010]; $J$ || [001] and $H$ || [100] the $MR$ again shows a behavior different from the corresponding case in CeRhAl$_4$Si$_2$. At 2 K the $MR$ rises monotonically reaching 44 and 115 %, respectively at 14 Tesla. The latter value is even larger than the peak value for $H$ || [001].

The sharp upturn in the $MR$ at spin flop and the associated hysteresis shift to lower fields as the temperature is increased (Figs. 6 (a) and 6 (b)). Above the spin-flop the $MR$ in two compounds shows opposite behavior with the variation in temperature. At 4, 6 and 10 K the $MR$ in CeRhAl$_4$Si$_2$ above 6 T becomes less negative than its corresponding values at 2 K. On the other hand in CeIrAl$_4$Si$_2$ the $MR$ at and above 5 K at high fields becomes
FIG. 7: (Color online) (a) A comparison of MR data of CeIrAl$_4$Si$_2$ and LaIrAl$_4$Si$_2$, (b) shows the $MR$ of the La compound at 2 K for $H$ along $[100]$ and $[001]$, respectively. (c) shows the $MR$ at selected temperature for $H \parallel [010]$ (b) and temperature (c) dependence of $MR(H)$ of nonmagnetic analogue LaIrAl$_4$Si$_2$.

less positive compared to the corresponding values at 2 K, and it even becomes negative at 10 K and above. Close to and above $T_{N1}$ and above the $MR$ is negative at all fields in both compounds.

The $MR$ in CeRhAl$_4$Si$_2$ at selected temperatures, for fields applied in the $ab$-plane, i.e. along $[100]$ and $[010]$ is qualitatively similar for current density parallel to $[001]$ and $[100]$, respectively. A relatively sharp upturn in $MR$ is seen at 5 and 8 K around $\sim 12$ and $\sim 6$ T, respectively, which is most likely arising from changes in the spin reorientation. In CeIrAl$_4$Si$_2$, for $J \parallel [001]$ and $H \parallel [100]$, we observe a step like feature, beginning around 8 T, in the $MR$ at 10 K data; however no corresponding anomaly is clearly seen in the magnetization. It may be recalled that a very weak hysteresis is seen at 8 K (Fig. 2(d)). Similarly, for $J \parallel [100]$ and $H \parallel [010]$, $MR$ shows some peculiar features. A field induced hysteresis appears at 5 K around 13 T, which splits into two at 8 and 10 K but vanishes again at 12 K. In Fig. 7 $MR$ data of CeIrAl$_4$Si$_2$ and LaIrAl$_4$Si$_2$ is compared. The $MR$ of La-analogue does not depend much upon direction as well as temperature in contrast to the magnetically ordered Ce-analogue. Above the spin-flop transition the $MR$ of both (i.e. Ce and La analogue) are nearly the same.

To summarize our results on $MR$, while there is a close correlation between the changes seen in the $MR$ and isothermal magnetization, some additional features seen in the directional dependence of $MR$ in the two compounds suggest differences in their Fermi surface topology. It would be of interest to calculate the band structure of these two compounds.
FIG. 8: (Color online) Heat capacity and calculated entropy as a function of temperature of CeRhAl$_4$Si$_2$ (left panels) and CeIrAl$_4$Si$_2$ (right panels). The heat capacity of La analogs are also plotted. The inset in (a) and (b) show the low temperature data of Ce compounds as $C/T$ vs. $T^2$.

E. Heat Capacity

The heat capacity of CeRh(Ir)Al$_4$Si$_2$ was measured between 100 mK and 150 K to gain more information about the magnetically ordered Kondo lattice state such as the entropy associated with the magnetic ordering, values of the coefficient of the linear term in the electronic heat capacity $\gamma$, which is proportional to enhanced electron effective mass, and Kondo temperature. The heat capacity of nonmagnetic analogs LaRh(Ir)Al$_4$Si$_2$ was also measured between 2 and 150 K. The data are plotted in Fig. 8. The heat capacity clearly exhibits two peaks in both compounds (Figs. 8 (a) and 8(b)) confirming the occurrence of two bulk phase transitions. The peak temperatures are overall in good agreement with the corresponding peaks in the susceptibility. For CeIrAl$_4$Si$_2$ the heat capacity was also measured in 5 and 8 T. The two peaks shift to lower temperatures in 5 T and they virtually disappear in 8 T above the spin-flop field where the field induces a ferromagnetic state.

The heat capacity data of La analog is typical of a nonmagnetic reference compound. The plots of $C/T$ vs. $T^2$ below 5 K for the two La-compounds (not shown) are linear and
a fit of the standard expression $C/T = \gamma + \beta T^2$, where $\gamma$ and $\beta$ are the electronic and phononic part of the heat capacity, furnishes the following values, $\gamma = 8.7$ and $8.0$ mJ/mol K$^2$, $\beta = 0.22$ and $0.21$ mJ/mol K$^4$ for the Rh and Ir compounds, respectively. The 4f-derived entropy $S_{4f}$ was calculated by following relation:

$$S_{4f} = \int \frac{C_{4f}}{T} dT$$

$C_{4f}$ was obtained by subtracting the heat capacity of the La-analog from the corresponding Ce-compound and making the usual assumption of lattice heat capacity being identical for the isotypic La and Ce compounds. Only 64% (69%) of entropy $S_{4f}$ for a doublet ground state with effective spin 1/2 (i.e. $Rln2$) is released up to $T_{N1}$ for CeRh(Ir)Al$_4$Si$_2$ indicating the presence of Kondo interaction in these materials, assuming insignificant short range order above $T_{N1}$. The entropy corresponding to full doublet ground state is recovered at temperature $\sim 32$ K (31 K).

The Kondo behavior of resistivity together with the reduced value of entropy at the magnetic transition temperature $T_m$ imply a partial quenching of the 4f-derived Ce magnetic moment by the Kondo interaction. In such cases the degeneracy of the ground state doublet is partially removed by the Kondo effect, and it has been shown that $S_{4f}(T_m) = S_K(T_m/T_K)$, where $S_{4f}$ is the entropy associated with the magnetic ordering and $S_K$ is the entropy at $T_m$ due to the Kondo effect with the Kondo temperature of $T_K$. The specific heat and the entropy as a function of $T/T_K$ for a spin 1/2 Kondo impurity is known, and the ratio $T_m/T_K$ can be determined using the value of $S_{4f}$. Using this procedure we get a single-ion Kondo temperature $T_K$ of 14 and 10 K in CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$, respectively. On the other hand if $T_m$ is taken as the temperature at which the upturn in the heat capacity begins than $T_K$ of 12.3 and 7.7 K are obtained. The Kondo temperature of a lattice is believed to be lower than its value for a single impurity. The simple analysis presented here supports the picture of two magnetically ordered compounds with a residual weak Kondo interaction with a Kondo temperature or lower than the magnetic ordering temperature. It may also be noticed that the $T_K$ of the Ir compound is lower than that of the Rh analog. This suggests larger electron correlation effect in CeRhAl$_4$Si$_2$, which is amply confirmed by the low temperature heat capacity data discussed below.

The heat capacity below 1 K down to 100 mK is shown in the insets of Figs. 8(a) and (b). An extrapolation of the data to $T = 0$ K gives $\gamma = 195.6$ and 49.4 mJ/mol K$^2$ in the Rh
and its Ir-sibling. The values of $\gamma$ are an order of magnitude larger than the corresponding values in the La-analog and imply a moderate enhancement of the effective electron masses due to the residual Kondo interaction in these two compounds. The magnetic part of the heat capacity in both CeRh(Ir)Al$_4$Si$_2$ show a broad hump at around 70-80 K indicating a Schottky anomaly due to the splitting of $2J + 1$ degenerate levels. This Schottky anomaly is discussed in the next section.

IV. DISCUSSION

The experimental data presented above show unequivocally that CeTAl$_4$Si$_2$ $(T = \text{Rh, Ir})$ compounds undergo antiferromagnetic ordering at low temperatures. Furthermore, the magnetization measurements revealed a reduced moment of $\sim 1 \mu_B/\text{Ce}$ which is much less compared to the free ion value of $g_J(= 6/7 \times 5/2)$, 2.14 $\mu_B/\text{Ce}$. This fact together with a large negative paramagnetic Weiss temperature $\theta_p$, the negative logarithmic increase of resistivity, reduced heat capacity jump and a relatively large Sommerfeld coefficient, clearly indicate significant influence of Kondo and crystal electric field (CEF) effects. To gain more insight into the Kondo and CEF effects, we have performed a CEF analysis on the magnetization and heat capacity data based on a point charge model. The Ce-atom in CeTAl$_4$Si$_2$ occupies the 1$b$-Wyckoff’s position and hence possesses the $4/mmm$ ($D_{4h}$) tetragonal point symmetry. For half integral spin of $J(= 5/2)$, the crystal field potential will split the $2J + 1(= 6)$ degenerate levels into three doublets. The CEF Hamiltonian for the Ce-atom in a tetragonal site symmetry is given by,

$$\mathcal{H} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4,$$  \hspace{1cm} (2)

where $B_i^m$ and $O_i^m$ are the CEF parameters and the Stevens operators, respectively. Here we have ignored the 6-th order Stevens operators in the Hamiltonian as they are zero for $J = 5/2$.

In the molecular field approximation, the total susceptibility $\chi$ is expressed in terms of the CEF susceptibility $\chi_{\text{CEF}}$ and the molecular field constant $\lambda$ as,

$$\frac{1}{\chi_i} = \frac{1}{\chi_{\text{CEF}}} - \lambda_i.$$

(3)
TABLE III: Crystal field parameters, molecular field constant and the energy levels for CeTAl$_4$Si$_2$ (T = Rh and Ir) obtained from the CEF fitting to the inverse susceptibility plot

|                  | CeRhAl$_4$Si$_2$ | CeIrAl$_4$Si$_2$ |
|------------------|------------------|------------------|
| $B^0_2$ (K)      | -6.52            | -1.40            |
| $B^0_4$ (K)      | -0.63            | -0.43            |
| $B^4_4$ (K)      | 4.74             | 6.34             |
| $\lambda_{[100]}$ (mol/emu) | -122             | -126             |
| $\lambda_{[001]}$ (mol/emu) | -45              | -5               |
| $\Delta_1$ (K)  | 136              | 120              |
| $\Delta_2$ (K)  | 342              | 361              |

The $\chi_{\text{CEF}}$ is given by the standard susceptibility expression, by the combination of Curie term and the Vanvleck term Ref. 15. It is to be mentioned here that the effective moment $\mu_{\text{eff}}$ along both the directions are slightly deviated from the standard value of 2.54 $\mu_B$/Ce, for a cerium atom in its trivalent state. Hence, while performing CEF analysis on the magnetic susceptibility data, we have plotted the inverse susceptibility plot in the form of $1/(\chi - \chi_0)$, where $\chi_0$ is determined from the modified Curie-Weiss law: $\chi = \chi_0 + C/(T - \theta_p)$ by fixing the effective magnetic moment to 2.54 $\mu_B$/Ce. A similar kind of approach has been made on previous occasions as well 16,17. Fig. 9(a) and (b) shows the calculated CEF magnetic susceptibility which explains the anisotropy reasonably well. Although it is possible to achieve a better fit to the experimental data, we have chosen the crystal field parameters in such a way that the crystal field energy levels thus obtained by diagonalizing the crystal field Hamiltonian Eq. 2 explains the Schottky heat capacity to be discussed later. The crystal field parameters, molecular field constants and the crystal field split energy levels are listed in Table III. It is to be noted here that the molecular field constant $\lambda$ is very large and highly anisotropic similar to that of the paramagnetic Weiss temperature $\theta_p$ as mentioned earlier. This large value of the molecular field $\lambda$ may be attributed to anisotropic magnetic exchange interactions and due to Kondo effect.

The value of the exchange constant $J_{\text{ex}}$ can be extracted from the crystal field parameter $B^0_2$ and the paramagnetic Weiss temperature. According to the mean field theory, $B^0_2$ and
FIG. 9: (Color online) (a) and (b) Inverse susceptibility plot of CeRhAl$_4$Si$_2$ and CeIrAl$_4$Si$_2$ and the calculated CEF susceptibility. The CEF energy levels are also shown. (c) and (d) Isothermal magnetization measure at $T = 2$ K and the calculated magnetization curve based on the CEF model. The dashed curve are the CEF magnetization multiplied by a factor (see text for details).

$\mathcal{J}_{ex}$ are given by the following expression\cite{20}:

$$
\theta_{p}^{[100]} = \frac{J(J+1)}{3k_B} \mathcal{J}_{ex}^{[100]} \frac{(2J-1)(2J+3)}{10k_B} B_2^0, \quad (4)
$$

$$
\theta_{p}^{[001]} = \frac{J(J+1)}{3k_B} \mathcal{J}_{ex}^{[001]} \frac{(2J-1)(2J+3)}{5k_B} B_2^0. \quad (5)
$$

The estimated values of $\mathcal{J}_{ex}$ for both the principal crystallographic directions are listed in Table IV. The negative value of $\mathcal{J}_{ex}$ simply implies the antiferromagnetic interaction of the $4f$ moments in these compounds. The exchange interaction is also highly anisotropic similar to the molecular field constant and it decreases along the [001] direction when the transition metal is changed from Rh to Ir. We have also calculated the isothermal magnetization based on the CEF model with the following Hamiltonian:

$$
\mathcal{H} = \mathcal{H}_{CEF} - g_{\mu_B} J_i H, \quad (6)
$$
TABLE IV: Anisotropic paramagnetic Weiss temperature obtained by fitting the inverse susceptibility to modified Curie-Weiss expression by fixing $\mu_{\text{eff}}$ to 2.54 $\mu_B/$Ce, $B_2^0$ parameter and the exchange interaction $J_{\text{ex}}$.

|               | $\theta^{[100]}_p$ (K) | $\theta^{[001]}_p$ (K) | $B^0_2$ (K) | $J^{[100]}_{\text{ex}}/k_B$ (K) | $J^{[001]}_{\text{ex}}/k_B$ (K) |
|---------------|------------------------|------------------------|------------|-------------------------------|-------------------------------|
| CeRhAl$_4$Si$_2$ | -140                   | -7.21                  | -6.52      | -40.93                        | -16.78                        |
| CeIrAl$_4$Si$_2$ | -125                   | -4.92                  | -1.40      | -41.27                        | -5                             |

where $H_{\text{CEF}}$ is given by Eq. 2, the second term is the Zeeman term. The magnetization $M_i$ is given by the following expression:

$$M_i = g_i \mu_B \sum_n |\langle n|J_i|n\rangle| \frac{\exp(-\beta E_n)}{Z}, \quad (i = x, y, z).$$

(7)

The calculated CEF magnetization is shown in Fig. 9(c) and (d) as solid lines. It is obvious from the figure that the CEF calculated magnetization are higher than that of the experimental curves, but still much smaller than the saturation value of $g_3J = (2.14 \mu_B/$Ce). Furthermore, if the calculated magnetization are multiplied by a factor of 0.57, for CeRhAl$_4$Si$_2$, then the theoretical curves are matching with the experimental data. On the other hand, the calculated CEF magnetization of CeIrAl$_4$Si$_2$ $H \parallel [001]$ matches with the experimental data while for $H \parallel [100]$, the calculated CEF has to be multiplied by a factor 0.36 to match with the experimental data. This multiplication factor of 0.57 for CeRhAl$_4$Si$_2$ along both the crystallographic directions and 0.36 for CeIrAl$_4$Si$_2$ along [100] direction is tentatively attributed to the Kondo effect. In the case of the rare-earth atom occupying the tetragonal site symmetry, the sign of the $B^0_2$ parameter usually determines the easy axis or easy plane of magnetization[19]. Here the sign of $B^0_2$ is negative which indicates that [001] direction is easy axis of magnetization which is consistent with our experimental data.

Another estimate of the Kondo temperature has been obtained from the magnetic part of the heat capacity. In a typical Kondo lattice system, the magnetic part of the heat capacity can be thought to be the combination of the Kondo and Schottky contributions, which can be expressed as:

19
\[ C_{4f} = C_K + C_{Sch}. \] (8)

The expression for \( C_K \) is given by Schotte and Schotte\(^{20}\) where they assumed a Lorentzian like density of states at the Fermi energy for the impurity spins \( S = 1/2 \):

\[ C_K = k_B \frac{\Delta}{\pi k_B T} \left( 1 - \frac{\Delta}{2\pi k_B T} \psi' \left( \frac{1}{2} + \frac{\Delta}{2\pi k_B T} \right) \right), \] (9)

where \( \psi' \) is the first derivative of digamma function. Here \( \Delta \) is the width of the Lorentzian and is assumed to be approximately the size of the Kondo energy \( k_B T_K \). For a three level system \( C_{Sch} \) is given by the expression:

\[
C_{Sch} = \left[ \frac{R}{(k_B T)^2} \frac{e^{(\Delta_1 + \Delta_2)/k_B T} \left[ -2\Delta_1 \Delta_2 + \Delta_2^2 (1 + e^{\Delta_1/k_B T}) + \Delta_1^2 (1 + e^{\Delta_2/k_B T}) \right]}{(e^{\Delta_1/k_B T} + e^{\Delta_2/k_B T} + e^{(\Delta_1 + \Delta_2)/k_B T})^2} \right], \] (10)

where \( R \) is the universal gas constant and \( \Delta_1 \) and \( \Delta_2 \) are the crystal field split excited energy levels. Using the energy levels obtained from the point charge model of the susceptibility data we have analyzed the magnetic part of the heat capacity using Eq. 8.

The solid line in Fig. 10 shows the combined contribution from the Kondo and the Schottky heat capacity. It is evident from the figure that the magnetic part of the heat capacity is reasonably well explained by Eq. 8. The Kondo temperature \( T_K \) thus obtained is 20 K for CeRhAl\(_4\)Si\(_2\) and 5 K for CeIrAl\(_4\)Si\(_2\), which are comparable to the values obtained using the procedure of Mori et al.\(^{11}\) A larger value of \( T_K \) implies a reduced jump in the heat capacity. If we refer to Fig. 10, the jump in the \( C_{4f} \) at the magnetic ordering temperature is smaller for CeRhAl\(_4\)Si\(_2\) compared to that of CeIrAl\(_4\)Si\(_2\) which has a lower \( T_K \). Our crystal field calculations on the magnetic susceptibility and heat capacity data clearly indicate that CeTAl\(_4\)Si\(_2\) (\( T = \text{Rh and Ir} \)) are Kondo lattice systems.

V. CONCLUSION

We have successfully synthesized single crystals of CeTAl\(_4\)Si\(_2\) (\( T = \text{Rh and Ir} \)) by using the Al-Si binary eutectic composition as flux. The grown crystals were having platelet like morphology with (001)-plane perpendicular to the plane of the crystal. The thermal and transport studies on these systems reveal that both the compounds order antiferromagnetically with two Néel temperatures. A sharp metamagnetic transition is observed for
FIG. 10: (Color online) The 4f contribution to the heat capacity $C_{4f}$. The thick solid line is sum of the Kondo and Schottky contribution, dashed line is the Kondo contribution $C_K$ and dashed-dotted line is due to the Schottky contribution $C_{Sch}$. The Schottky energy levels are also shown.

$H \parallel [001]$ direction where as the magnetization is relatively small and varies linearly for $H \parallel [100]$ direction, indicating that $[001]$ direction is the easy axis of magnetization in both the cases. A large negative paramagnetic Weiss temperature $\theta_p$, a reduced magnetization value, a reduced magnetic entropy and a negative logarithmic increase in the resistivity clearly indicates that these systems are Kondo lattice systems. We have performed a detailed crystal electric field calculations on the magnetization and heat capacity data and estimated the energy levels of the $2J + 1$ degenerate ground state. Similarly, an estimate of the Kondo temperature and exchange interaction has also been made. It is found from our analysis that exchange interaction is anisotropic and the Kondo temperature is larger for Rh system while it is smaller for the Ir system.

Note added in Proof: While this manuscript was under preparation, Ghimire et al.\textsuperscript{[21]} have reported the anisotropic susceptibility and resistivity, and the low temperature heat capacity (1.8 to 30 K) of CeMAl$_4$Si$_2$ ($M = $ Rh, Ir, Pt) compounds\textsuperscript{[21]}. Our observation of two antiferromagnetic transitions in these two compounds ($M = $ Rh and Ir) is in conformity with their results. Ghimire et al. allude to the presence of Kondo interaction and the opportunity
to explore strongly correlated electron behaviour in these quaternary compounds. Our low temperature heat capacity data (below 1 K) reveal moderately heavy electron masses and preliminary resistivity data at 23 kbar in CeIrAl$_4$Si$_2$ show pressure induced decrease of $T_N$, which is a standard feature of Kondo lattices predicted by the Doniach phase diagram$^{10}$. Our more extensive magnetization data, and magnetoresistivity reveal some additional features in the properties of the these two compounds. However, while we observe a Kondo behavior in the resistivity of our samples, Ghimire et al. report a normal temperature dependence in their samples. The intrinsic Kondo nature of our samples is further supported by our preliminary resistivity data at 23 kbar in CeIrAl$_4$Si$_2$ showing pressure induced decrease of $T_N$, which is a standard feature of Kondo lattices predicted by the Doniach’s phase diagram.

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