Ferromagnetic cluster-glass phase in Ca(Co1-xIr)(2-y)As-2 crystals

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Ferromagnetic cluster-glass phase in Ca(Co\(_{1-x}\)Ir\(_x\))\(_{2-y}\)As\(_2\) crystals

Abstract

Single crystals of Ca(Co\(_{1-x}\)Ir\(_x\))\(_{2-y}\)As\(_2\) with 0 \(\leq x \leq 0.35\) and 0.10 \(\leq y \leq 0.14\) have been grown using the self-flux technique and characterized by single-crystal x-ray diffraction (XRD), energy-dispersive x-ray spectroscopy, magnetization M, and magnetic susceptibility \(\chi\) measurements versus temperature T, magnetic field H, and time t, and heat-capacity \(C_p(H,T)\) measurements. The XRD refinements reveal that all the Ir-substituted crystals crystallize in a collapsed-tetragonal structure as does the parent CaCo\(_{2-y}\)As\(_2\) compound. A small 3.3% Ir substitution for Co in CaCo1.86As2 drastically lowers the A-type antiferromagnetic (AFM) transition temperature TN from 52 to 23 K with a significant enhancement of the Sommerfeld electronic heat-capacity coefficient. The A-type AFM structure consists of ab-plane layers of spins ferromagnetically aligned along the c axis with AFM alignment of the spins in adjacent layers along this axis. The positive Weiss temperatures obtained from Curie-Weiss fits to the \(\chi(T > T_N)\) data indicate that the dominant magnetic interactions are ferromagnetic (FM) for all x. A magnetic phase boundary is inferred to be present between \(x = 0.14\) and \(x = 0.17\) from a discontinuity in the x dependencies of the effective moment and Weiss temperature in the Curie-Weiss fits. FM fluctuations that strongly increase with increasing x are also revealed from the \(\chi(T)\) data. The magnetic ground state for \(x \geq 0.17\) is a spin glass as indicated by hysteresis in \(\chi(T)\) between field-cooled and zero-field-cooled measurements and from the relaxation of M in a small field that exhibits a stretched-exponential time dependence. The spin glass has a small FM component to the ordering and is hence inferred to be comprised of small FM clusters. The competing AFM and FM interactions along with crystallographic disorder associated with Ir substitution are inferred to be responsible for the development of a FM cluster-glass phase. A logarithmic T dependence of \(C_p\) at low T for \(x = 0.14\) is consistent with the presence of significant FM quantum fluctuations. This composition is near the T=0 boundary at \(x = 0.16\) between the A-type AFM phase containing ferromagnetically-aligned layers of spins and the FM cluster-glass phase.

Disciplines

Condensed Matter Physics
Ferromagnetic cluster-glass phase in Ca(Co\textsubscript{1\textminus}x)Ir\textsubscript{x}As\textsubscript{2} crystals

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Single crystals of Ca(Co\textsubscript{1\textminus}x)Ir\textsubscript{x}As\textsubscript{2} with 0 ≤ x ≤ 0.35 and 0.10 ≤ y ≤ 0.14 have been grown using the self-flux technique and characterized by single-crystal x-ray diffraction (XRD), energy-dispersive x-ray spectroscopy, magnetization M, and magnetic susceptibility χ measurements versus temperature T, magnetic field H, and time t, and heat-capacity C\textsubscript{p}(H, T) measurements. The XRD refinements reveal that all the Ir-substituted crystals crystallize in a collapsed-tetragonal structure as does the parent CaCo\textsubscript{2}As\textsubscript{2} compound. A small 3.3\% Ir substitution for Co in CaCo\textsubscript{1.97}As\textsubscript{2} drastically lowers the A-type antiferromagnetic (AFM) transition temperature T\textsubscript{N} from 52 to 23 K with a significant enhancement of the Sommerfeld electronic heat-capacity coefficient. The A-type AFM structure consists of ab-plane layers of spins ferromagnetically aligned along the c axis with AFM alignment of the spins in adjacent layers along this axis. The positive Weiss temperatures obtained from Curie-Weiss fits to the χ(T > T\textsubscript{N}) data indicate that the dominant magnetic interactions are ferromagnetic (FM) for all x. A magnetic phase boundary is inferred to be present between x = 0.14 and x = 0.17 from a discontinuity in the x dependencies of the effective moment and Weiss temperature in the Curie-Weiss fits. FM fluctuations that strongly increase with increasing x are also revealed from the χ(T) data. The magnetic ground state for x ≥ 0.17 is a spin glass as indicated by hysteresis in χ(T) between field-cooled and zero-field-cooled measurements and from the relaxation of M in a small field that exhibits a stretched-exponential time dependence. The spin glass has a small FM component to the ordering and is hence inferred to be comprised of small FM clusters. The competing AFM and FM interactions along with crystallographic disorder associated with Ir substitution are inferred to be responsible for the development of a FM cluster-glass phase. A logarithmic T dependence of C\textsubscript{p} at low T for x = 0.14 is consistent with the presence of significant FM quantum fluctuations. This composition is near the T = 0 boundary at x ≈ 0.16 between the A-type AFM phase containing ferromagnetically-aligned layers of spins and the FM cluster-glass phase.

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I. INTRODUCTION

Since the discovery of high-T\textsubscript{c} superconductivity (SC) in doped iron arsenides \textit{A}Fe\textsubscript{2}As\textsubscript{2} (A = Ca, Sr, Ba, Eu), the interplay between magnetism and SC in these materials opened up new research areas [1–10]. Ternary arsenide compounds having the general formula AM\textsubscript{2}As\textsubscript{2} (M = transition metal) commonly crystallize in the layered body-centered-tetragonal ThCr\textsubscript{2}Si\textsubscript{2}-type crystal structure. Here M\textsubscript{2}As\textsubscript{2} layers are comprised of edge-sharing MAs\textsubscript{4} tetrahedra and the A atoms occupy layers between the M\textsubscript{2}As\textsubscript{2} layers. Depending on the ratio c/a of the tetragonal c and a lattice parameters, a compound can crystallize in either the collapsed-tetragonal (cT) or uncollapsed-tetragonal (ucT) version of the structure or in the crossover regime [11–14]. Electron and/or hole doping in the three different atomic sites have been reported to introduce superconducting and/or magnetic phenomena in these materials. Fe-based arsenide compounds have been extensively studied after the discovery of SC at T\textsubscript{c} = 38 K in K-doped BaFe\textsubscript{2}As\textsubscript{2} in 2008 [1]. Both hole doping and electron doping subsequently resulted in the observation of SC in the AFe\textsubscript{2}As\textsubscript{2} (A = Sr, Ca, and Eu) systems [15–18]. In these systems, SC is realized by suppressing the long-range antiferromagnetic (AFM) order of the parent compounds through chemical substitution or by the application of pressure. Later it was found that the suppression of long-range AFM order while preserving strong dynamic short-range AFM correlations was required for SC to appear, indicating that AFM fluctuations are required for the appearance of SC in the iron arsenides [2–4,6–10]. The self-doped alkali-metal compounds KFe\textsubscript{2}As\textsubscript{2} (T\textsubscript{c} = 3.8 K), RbFe\textsubscript{2}As\textsubscript{2} (T\textsubscript{c} = 2.6 K), and CsFe\textsubscript{2}As\textsubscript{2} (T\textsubscript{c} = 2.6 K) also exhibit SC [15,19,20]. These discoveries sparked interest in studying other transition-element-based analogs of this family of materials.

Metallic ThCr\textsubscript{2}Si\textsubscript{2}-type CoAs-based compounds exist but so far do not exhibit SC. However, these materials have attracted significant interest due to their peculiar itinerant magnetic behavior arising from their electronic structure and sensitivity to chemical substitution. For example, metallic BaCo\textsubscript{2}As\textsubscript{2} has an ucT structure and does not exhibit long-range magnetic ordering down to a temperature T = 1.8 K [21,22]. However, crystals of this compound have a rather large magnetic susceptibility χ with a broad maximum followed by a weak low-temperature upturn [21]. A large exchange-enhanced density of states at the Fermi energy D(E\textsubscript{F}) ≈ 18 states/eV f.u. was estimated for the material.
from low-\textit{T} heat-capacity data, where f.u stands for formula unit [22]. In the initial report, it was argued that long-range ferromagnetic (FM) ordering is suppressed by quantum fluctuations [21], although a subsequent study [22] showed that the properties of BaCo$_2$As$_2$ are not very sensitive to chemical doping.

On the other hand, SrCo$_2$As$_2$ crystallizes in the \textit{ucT} structure and CaCo$_2$-As$_2$ crystallizes in the \textit{ct'} structure [14,16,23–25]. Metallic SrCo$_2$As$_2$ is a Stoner-enhanced paramagnet with no long-range magnetic ordering or SC at temperatures above 0.05 K [26]. Inelastic neutron-scattering measurements revealed the presence of stripe-type AFM fluctuations at the same wave vector as observed for the high-\textit{T}$_c$ parent compounds AF$_2$As$_2$ [26,27]. However, in contrast to the AF$_2$As$_2$ compounds, no obvious Fermi-surface nesting was observed at that wave vector for SrCo$_2$As$_2$ and, furthermore, FM fluctuations occur that evidently hinder the occurrence of SC [28,29]. FM fluctuations were also observed in FeAs-based superconductors, suggesting that the different $T_c$'s observed in these materials may be at least partially explained by different levels of FM fluctuations in the compounds [30].

In contrast to BaCo$_2$As$_2$ and SrCo$_2$As$_2$, a detectable concentration of vacancies is observed on the Co sites in CaCo$_{1-x}$As$_2$; that undergoes A-type AFM ordering with propagation vector $\bar{\tau} = (0, 0, 1)$ at $T = 52–77$ K, depending on the crystal [25,31,32]. In this magnetic structure, the ordered moments on the Co sites within the \textit{ab} plane are ferromagnetically aligned along the $c$ axis with AFM alignment between adjacent planes. FM interactions dominate together with relatively weak AFM interactions between Co planes responsible for the A-type AFM ordering. Inelastic neutron-scattering experiments reveal the presence of strong magnetic frustration in the system within the \textit{J}_1-\textit{J}_2 Heisenberg model on a square lattice with the nearest-neighbor exchange interaction being FM [33]. This strong magnetic frustration establishes CaCo$_{1-x}$As$_2$ as a unique member of the ternary arsenide family.

Chemically-doped Co-based arsenides are of significant interest due to the interplay between the lattice, electronic, and magnetic degrees of freedom. For example, the K-doped compound Ba$_{0.94}$K$_{0.06}$Co$_2$As$_2$ shows weak FM behavior; however, the magnetic behavior of the composition Ba$_{0.78}$K$_{0.22}$Co$_2$As$_2$ is found to be quite similar to that observed for undoped BaCo$_2$As$_2$ [22]. This difference has been suggested to be due to different Co defect levels associated with the crystal growth.

It has also been discovered that the system Ca$_{1-x}$Sr$_x$Co$_{2-y}$As$_2$ exhibits a composition-induced crossover in the magnetic anisotropy [34,35]. In the region 0 $\leq$ $x$ $\leq$ 0.2, the compounds order in the A-type AFM structure where the moments are aligned along the $c$ axis as in CaCo$_{2-y}$As$_2$. At temperature $T = 5$ K and 0.2 $\leq$ $x$ $\leq$ 0.3, the moments are still aligned along the $c$ axis but with a + + + + + + configuration with propagation vector $\bar{\tau} = (0, 0, 1/2)$ [36]. For compositions 0.3 $\leq$ $x$ $\leq$ 0.5, the ordered moments also have the propagation vector $\bar{\tau} = (0, 0, 1/2)$ but with the moments now aligned in the \textit{ab} plane with either a + + + + + order or a $\text{90}^{\circ}$ helix AFM configuration along the $c$ axis [36]. Finally, for $x$ $\leq$ 0.5, the material exhibits no magnetic transitions above 2 K. It was concluded from theoretical modeling of the structures obtained from the neutron-diffraction measurements that single-ion magnetic anisotropy and frustration of AFM nearest- and next-nearest-layer exchange interactions are all composition dependent in Ca$_{1-x}$Sr$_x$Co$_{2-y}$As$_2$ [36]. The composition $x = 0.33$ exhibits a temperature-induced transition between moment alignments in the \textit{ab} plane and along the \textit{c} axis [35].

Recently, non-Fermi-liquid types of behavior associated with a composition-induced magnetic quantum-critical point in Sr(Co$_1$-$_x$Ir$_x$)$_2$As$_2$ crystals near $x = 0.3$ has been reported [37]. In addition, crystals of Sr(Co$_1$-$_x$Ni$_x$)$_2$As$_2$ with 0 $< x$ $< 0.3$ exhibit $c$-axis helical or spin-density-wave AFM ordering [37–39], which is quite unusual in itinerant antiferromagnets. A small amount (2.5\%) of La doping has been reported to cause FM ordering in Sr$_{1-x}$La$_x$Co$_2$As$_2$ [40,41]. In CaCo$_{2-y}$As$_2$, the A-type AFM order was found to be smoothly suppressed by Fe doping on the Co site [42].

The above studies illustrate the impact of chemical substitution/doping on the physical properties exhibited by the Co$_{12}$ systems. Since the alkaline-earth Co-As systems exhibit itinerant magnetism that originates from the properties of band electrons near the Fermi surface, the magnetic properties strongly depend on the electronic effects of substituting/doping by different elements. Most such studies have been carried out using 3$d$- and 4$d$-transition metal substitutions on the Co sites, and the effect of substituting 5$d$ atoms for Co has not been emphasized. Moreover, the high atomic number of 5$d$ elements is expected to significantly alter the magnetic interaction in those systems due to the strong spin-orbit coupling associated with such atoms. Spin-orbit coupling has been considered to be an important tool to tune the superconducting and magnetic properties of different systems [43–48]. Thus, it is interesting to examine whether 5$d$-element substitutions on the Co site can reveal novel properties and ground states.

In this paper, we report the influence of Ir (5$d$) substitutions for Co in CaCo$_{1.86}$As$_2$ on the crystallographic, magnetic, and thermal properties. Although all the Ca(Co$_{1-x}$Ir$_x$)$_2$-As$_2$ compounds are found to crystallize in the \textit{ct'} structure as in the parent compound, the Ir substitutions significantly alter the magnetic interactions in these systems. A composition-induced crossover from the A-type AFM state to a magnetically disordered FM cluster-glass state is observed. The $x = 0.14$ composition exhibits signatures of FM quantum fluctuations with a concomitant significant increase in the electronic Sommerfeld coefficient.

The experimental details are given in Sec. II. The crystallography results are presented in Sec. III, magnetization and magnetic susceptibility data in Sec. IV, a study of the magnetism of the glassy state in Sec. V, and the heat-capacity measurements in Sec. VI. A summary of the results is given in Sec. VII.

II. EXPERIMENTAL DETAILS

Single crystals of Ca(Co$_{1-x}$Ir$_x$)$_2$-As$_2$ with $x = 0$, 0.033, 0.065, 0.10, 0.14, 0.17, 0.25, and 0.35 were grown out of (Co,Ir)As self flux using the high-temperature solution-growth technique. The high-purity starting materials Ca (99.999%, Alfa Aesar), Co (99.998%, Alfa Aesar),
Compositions were estimated from EDS analyses. Also listed are the tetragonal lattice parameters $a$ and $c$, the unit cell volume $V_{cell}$, the $c/a$ ratio, and the fractional $c$-axis position of the As site ($z_{As}$) obtained from single-crystal XRD data.

| Compound          | $a$ (Å) | $c$ (Å) | $V_{cell}$ (Å$^3$) | $c/a$      | $z_{As}$ |
|-------------------|---------|---------|---------------------|------------|----------|
| CaCo$_{0.862}$As$_2$ | 3.9837(4) | 10.2733(4) | 163.04(9) | 2.5788(6) | 0.3672(4) |
| Ca$_{0.967}$Ir$_{0.033}$Co$_{0.862}$As$_2$ | 3.988(1) | 10.268(7) | 163.3(1) | 2.575(8) | 0.3665(1) |
| Ca$_{0.915}$Ir$_{0.085}$Co$_{0.862}$As$_2$ | 3.990(2) | 10.268(7) | 163.5(2) | 2.573(9) | 0.3664(2) |
| Ca$_{0.904}$Ir$_{0.096}$Co$_{0.862}$As$_2$ | 3.996(2) | 10.274(5) | 164.1(2) | 2.571(7) | 0.3662(2) |
| Ca$_{0.886}$Ir$_{0.114}$Co$_{0.862}$As$_2$ | 3.996(2) | 10.294(5) | 164.3(2) | 2.577(7) | 0.3672(2) |
| Ca$_{0.831}$Ir$_{0.169}$Co$_{0.862}$As$_2$ | 4.005(1) | 10.315(3) | 165.5(1) | 2.575(4) | 0.3677(2) |
| Ca$_{0.792}$Ir$_{0.202}$Co$_{0.862}$As$_2$ | 4.017(1) | 10.305(3) | 166.3(1) | 2.565(4) | 0.3681(2) |
| Ca$_{0.664}$Ir$_{0.354}$Co$_{0.862}$As$_2$ | 4.029(2) | 10.326(3) | 167.7(1) | 2.562(4) | 0.3684(2) |

Ir (99.999%, Ames Laboratory), and As (99.9999%, Alfa Aesar) were taken in the molar ratio Ca:Co:Ir:As = 1:4(1 − $x$):4$x$:4 and placed in an alumina crucible. The crucible was then sealed in a silica tube under ≈1/4 atm of Ar gas. Quartz wool was placed above the filled crucible to extract the flux during centrifugation. The assembly was preheated to 650 °C for 6 h and then heated to 1300 °C at 50 °C/h. The sample was kept at that temperature for 20 h for homogenization. Then the tube was cooled to 1180 °C at a rate of 6 °C/h and the single crystals were separated from the flux using a centrifuge. Shiny platelike single crystals of different sizes were obtained from the growths with the $c$ axis perpendicular to the plate surfaces. However, the crystal size and homogeneity both decreased with increasing Ir substitution, so we could not obtain crystals with $x > 0.35$.

The phase homogeneity and the average composition of the Ca(Co$_{1−x}$Ir$_x$)$_2$As$_2$ crystals were determined using a scanning-electron microscope equipped with an energy-dispersive x-ray spectroscopy (EDS) attachment from JEOL. The chemical compositions were measured at many points on both surfaces of the platelike crystals to confirm their chemical homogeneity. The average compositions of the crystals used for different measurements are listed in Table I. Generally, when the $c/a$ ratio is less than 2.67, the system is considered to form with a $cT$ crystal structure [14]. The $c/a$ values for the present crystals are well below that value indicating that all the Ir-substituted compositions in our study form in a $cT$ structure as does the undoped CaCo$_{1−x}$As$_2$ parent compound. The EDS results reveal that the vacancy concentration on the Co site changes from 7(1)% in the parent CaCo$_1$As$_2$ compound to 5(1)% with 35% Ir substitution. As a single-crystal XRD refinement does not allow for simultaneous refinement of the fraction Co/Ir and total occupation of the position, only the total occupancies were refined based on the Co/Ir ratio taken from the EDS data. The variation in the Ir content

### III. Crystallography

The room-temperature single-crystal XRD measurements demonstrated that the Ca(Co$_{1−x}$Ir$_x$)$_2$As$_2$ (0 ≤ $x$ ≤ 0.35) crystals form in the body-centered tetragonal ThCr$_2$Si$_2$-type crystal structure (space group $I4/mm$) shown in Fig. 1. The crystallographic parameters are listed in Table I. The unit cell parameters were refined using the program SHELXL-2014 [53] within the APEX3 software package.

![Unit cell of the body-centered tetragonal ThCr$_2$Si$_2$ crystal structure. The figure was drawn using VESTA [54].](image-url)

The $M(H, T)$ data were obtained using a Quantum Design, Inc., magnetic-properties measurement system SQUID magnetometer in the range $T = 1.8$ to 300 K with magnetic fields up to 5.5 T (1 T ≡ 10$^4$ Oe). The heat-capacity $C_p(H, T)$ measurements were performed using the relaxation technique in a Quantum Design, Inc., physical-properties measurement system in the ranges $T = 1.8$—300 K and $H = 0$—9 T.
within the crystals as reflected in the compositional error bars was found to be small for low Ir substitution levels. However, the inhomogeneity increases for 35% Ir-substituted crystals. The crystallographic parameters are plotted versus Ir concentration $x$. The lines are guides to the eye.

IV. MAGNETIC SUSCEPTIBILITY

The temperature dependence of the magnetization for Ca(Co$_{1-x}$Ir$_x$)$_{2-y}$As$_2$ crystals was measured under zero-field-cooled (ZFC) and field-cooled (FC) protocols in a magnetic field $H = 0.1$ T applied in the $ab$ plane ($H \parallel ab$) and along the $c$ axis ($H \parallel c$). Figures 3(a)–3(h) show the temperature dependence of the magnetic susceptibility $\chi \equiv M/H$ for all eight Ca(Co$_{1-x}$Ir$_x$)$_{2-y}$As$_2$ crystals. Evidence for some type of magnetic ordering is seen for each of the crystals. The details on the possible nature of the magnetic ground states are as follows.

A. Antiferromagnetic ordering temperature $T_N$ for $0 \leq x \leq 0.14$

The parent compound CaCo$_{1.86(2)}$As$_2$ orders in an A-type AFM structure at $T_N = 52(1)$ K as reported earlier [25], where $\chi_c(T \rightarrow 0) = 0$ and $\chi_{ab}$ is nearly independent of $T$ below $T_N$. These are the characteristic signatures of a $c$-axis collinear antiferromagnet. In this magnetic structure of CaCo$_{1.86(2)}$As$_2$, as noted above the ordered moments within an $ab$ plane are aligned ferromagnetically along the $c$ axis with the moments in adjacent layers along the $c$ axis aligned antiferromagnetically. Thus, $\chi(T)$ below $T_N$ is anisotropic with the $c$ axis as the easy axis.

Figure 4(a) shows expanded plots of $\chi_{ab}$ and $\chi_c$ versus $T$ for Ca(Co$_{1-x}$Ir$_x$)$_{2-y}$As$_2$ crystals with $x = 0$ to $x = 0.14$. For antiferromagnets with an easy $c$ axis as in CaCo$_{2-y}$As$_2$, the Neel temperature is the temperature of the peak in the derivative $d(\chi_c)/dT$ [55]. Plots of $d(\chi(T))/dT$ versus $T$ are shown in Fig. 4(b) where the $T_N$ values obtained from the temperatures of the peaks are listed in Table II. The $T_N$ decreases rapidly to 23(1) K for 3.3% Ir substitution.
Moreover, with increasing $x$, the magnitudes of both $\chi_{ab}$ and $\chi_c$ increase significantly below $T_N$, suggesting an increase in FM fluctuations. Interestingly, though the $\chi_c$ suggests an AFM ordering below 9.6 K for $x = 0.14$ (1), $\chi_{ab}$ does not show any peak/cusp/inflection at $T_N$ and increases monotonically for temperatures down to 2 K.

**B. Magnetic susceptibility in the paramagnetic state**

The $\chi(T)$ data in the paramagnetic (PM) state at $T > T_N$ are analyzed in terms of local moments using the modified Curie-Weiss law

$$\chi_\alpha(T) = \chi_0 + \frac{C_\alpha}{T - \theta_\alpha}, \quad (\alpha = ab, \ c), \quad (1)$$

where $\chi_0$ is an isotropic temperature-independent term that contains the diamagnetic contributions from the atomic cores and the conduction-carrier orbital Landau susceptibilities, together with the paramagnetic contribution from the Pauli spin susceptibility of the conduction carriers. The Curie constant $C_\alpha$ contains the diamagnetic contributions from the atomic cores and the conduction-carrier orbital Landau susceptibilities, together with the paramagnetic contribution from the Pauli spin susceptibility of the conduction carriers. The Curie constant

$$C_\alpha = \frac{N_A g_\alpha^2 S(S + 1)\mu_B^2}{3k_B} = \frac{N_A \mu_{\text{eff}}^2}{3k_B} \quad (\alpha = ab, \ c), \quad (2)$$

where $N_A$ is Avogadro’s number, $g_\alpha$ is the spectroscopic splitting factor (g factor), $S$ is the spin angular-momentum quantum number, $k_B$ is Boltzmann’s constant, and $\mu_{\text{eff}}$ is the effective moment of a spin in units of Bohr magnetons $\mu_B$. Inserting the Gaussian cgs values of the fundamental constants into Eq. (2), the Curie constant per mole of spins is expressed as

$$C_\alpha \approx \frac{\mu_{\text{eff}}^2}{8} (\mu_B/\text{f.u.}). \quad (3)$$

Hence

$$\mu_{\text{eff}} (\mu_B/\text{f.u.}) \approx \sqrt{8C_\alpha}. \quad (4)$$

The anisotropic inverse susceptibilities of the CaCo$_{0.83}$Ir$_{0.17}$As$_2$ crystals are plotted versus temperature in Fig. 5. The fitted parameters for the $\chi^{-1}(T)$ data in Fig. 5 obtained over the temperature range 150 K to 300 K using the modified Curie-Weiss law are listed in Table II. The fits are shown as the solid red curves in Fig. 5. The effective moment $\mu_{\text{eff}}$ and Weiss temperature $\theta_\alpha$ are plotted versus $x$ in Figs. 6(a) and 6(b), respectively.
TABLE II. Parameters obtained from modified Curie-Weiss fits to $\chi^{-1}(T)$ data between 150 and 300 K for Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ by using Eq. (1). Shown are the $T$-independent contributions to the susceptibility $\chi_0$, Curie constant per mol $C_0$ in $\alpha = ab, c$ directions, Weiss temperature $\theta_p$, and effective moment per formula unit (f.u.) $\mu_{\text{eff}} = \mu_0 H_{\text{SF}} / [\mu_0 (T - \theta_p)]$, calculated from Eq. (4). Also included are the Néel temperatures $T_N$ obtained from the temperatures of the cusps in $d(\chi, T)/dT$ in Fig. 4(b), the $ab$-plane spin-flop fields $H_{\text{SF}}$ at $T = 2$ K, and the blocking temperatures $T_B$.

| Compound                     | Field Orientation | $\chi_0$ for $(10^{-8}$ cm$^3$ mol$^{-1})$ | $C_0$ (cm$^3$ mol$^{-1}$ K$^{-1}$) | $\mu_{\text{eff}}$ (G) | $\theta_p$ (K) | $T_N$ (K) | $H_{\text{SF}}$ (kOe) | $T_B$ (K) |
|------------------------------|-------------------|--------------------------------------|---------------------------------|------------------------|--------------|------------|-----------------------|-----------|
| CaCo$_{1.86}$As$_2$          | $H \parallel ab$  | 0.03(2)                              | 0.354(7)                        | 1.68(2)                | 76(1)        | 53(5)      | 35.0(5)               |           |
|                              | $H \parallel c$   | -0.2(2)                              | 0.416(3)                        | 1.82(1)                | 75(1)        |            |                       |           |
| Ca(Co$_{0.967}$Ir$_{0.033}$)$_{1.86}$As$_2$ | $H \parallel ab$  | 5.8(2)                               | 0.308(8)                        | 1.57(2)                | 38(2)        | 23(5)      | 22.5(5)               |           |
|                              | $H \parallel c$   | 5.72(6)                              | 0.355(2)                        | 1.67(1)                | 34.8(5)      |            |                       |           |
| Ca(Co$_{0.935}$Ir$_{0.065}$)$_{1.86}$As$_2$ | $H \parallel ab$  | 3.58(3)                              | 0.316(4)                        | 1.59(1)                | 44.2(2)      | 16.5       | 17.5(1)               |           |
|                              | $H \parallel c$   | 3.39(5)                              | 0.357(4)                        | 1.69(1)                | 44.5(5)      |            |                       |           |
| Ca(Co$_{0.90}$Ir$_{0.10}$)$_{1.86}$As$_2$ | $H \parallel ab$  | 6.9(1)                               | 0.320(3)                        | 1.60(1)                | 38(1)        | 11.5       | 15.0(2)               |           |
|                              | $H \parallel c$   | 7.9(1)                               | 0.361(5)                        | 1.70(1)                | 42(1)        |            |                       |           |
| Ca(Co$_{0.86}$Ir$_{0.14}$)$_{1.87}$As$_2$ | $H \parallel ab$  | 1.9(2)                               | 0.310(7)                        | 1.57(2)                | 40(2)        | 9.6        | 5.0(1)                |           |
|                              | $H \parallel c$   | 2.61(5)                              | 0.322(2)                        | 1.60(1)                | 49(1)        |            |                       |           |
| Ca(Co$_{0.83}$Ir$_{0.17}$)$_{1.87}$As$_2$ | $H \parallel ab$  | 1.8(2)                               | 0.529(8)                        | 2.06(2)                | 65(1)        |            | 6.1                   |           |
|                              | $H \parallel c$   | 1.1(2)                               | 0.559(7)                        | 2.11(1)                | 65.4(9)      |            |                       |           |
| Ca(Co$_{0.75}$Ir$_{0.25}$)$_{1.89}$As$_2$ | $H \parallel ab$  | 2.4(2)                               | 0.686(6)                        | 2.34(1)                | 62.3(7)      |            | 5.5                   |           |
|                              | $H \parallel c$   | 2.5(4)                               | 0.716(12)                       | 2.39(2)                | 61(1)        |            |                       |           |
| Ca(Co$_{0.65}$Ir$_{0.35}$)$_{1.90}$As$_2$ | $H \parallel ab$  | 1.0(2)                               | 0.681(7)                        | 2.35(1)                | 65(1)        |            | 4.5                   |           |
|                              | $H \parallel c$   | 0.8(2)                               | 0.715(11)                       | 2.39(2)                | 64(1)        |            |                       |           |

For spins $S$ with $g = 2$, the isotropic Curie constant in units of cm$^3$ K/mol spins is

$$C = 0.5002S(S + 1).$$

The Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ system has approximately 1.9 transition-metal atoms per formula unit and assuming that the Co/Ir atoms carry a local moment, Eq. (5) gives

$$C_{\text{mol}} \approx 0.95S(S + 1),$$

per mole of Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ formula units. Thus if $S = 1/2$ with $g = 2$, we expect $C_{\text{mol}} \approx 0.74$ cm$^3$ K/mol, whereas $S = 1$ gives $C_{\text{mol}} \approx 1.80$ cm$^3$ K/mol. From Table II, the Curie constants are in the range 0.31–0.36 cm$^3$ K/mol for $0 \leq x \leq 0.14$ and 0.53–0.72 cm$^3$ K/mol for 0.17 $\leq x \leq 0.35$. Thus there is a significant change in the magnetic character of Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ between the composition ranges $0 \leq x \leq 0.14$ and $0.17 \leq x \leq 0.35$, suggesting the presence of a magnetic phase boundary at $x \approx 0.15$. In addition, the large discrepancy between the measured values for $x \leq 0.14$ and the values obtained from Eq. (6) suggests that the magnetism is itinerant for these compositions as previously deduced for $x = 0$ (see, e.g., Ref. [33]). On the other hand, the larger values of $C_{\text{mol}}$ for the range 0.17 $\leq x \leq 0.35$ compared with those at lower $x$ values suggests an increased local-moment character for $x \geq 0.17$.

C. Magnetization versus applied magnetic field isotherms

To further clarify the magnetic ground states in Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$, $M(H)$ isotherms were measured at different temperatures in the field range 0–5.5 T, as shown in Figs. 7(a)–7(g) for $H \parallel ab$ and Figs. 7(h)–7(n) for $H \parallel c$. The $M(H)$ behavior in both field directions is nonlinear up to a much higher temperature than their
characteristic temperature $T_N$ or $T_B$ due to the presence of short-range magnetic interactions. Figures 8(a)–8(h) show $M(H)$ isotherms at $T = 2$ K for different compositions with both field directions. Here $M_{ab}(H)$ for $x = 0$ increases linearly with $H$ whereas $M_c(H)$ clearly exhibits a spin-flop (SF) transition at $H_{SF} = 3.5$ T, similar to the results reported earlier [25]. However, the SF transition field rapidly decreases to $H_{SF} = 2.15(5)$ T for $x = 0.033$, while retaining a linear $M_{ab}(H)$ behavior up to $H = 5.5$ T. For both crystals, no tendency towards saturation was observed in either $M_{ab}(H)$ or $M_c(H)$ isotherms in the field region studied. The $H_{SF}$ decreases further with increasing $x$ and becomes negligible for $x = 0.14$. The jump in $M_c(H)$ at $H_{SF}$ also broadens with increasing $x$.

The magnetizations $M_{ab}(H)$ and $M_c(H)$ for $x = 0.065$ and 0.10 exhibit a saturation tendency at higher fields, suggesting a reduction of AFM interactions with increasing Ir concentration. The magnetic saturation tendency is observed at much lower $H$ for $x = 0.14$ and at the highest applied field the magnetization almost saturates to the saturation magnetizations $M_{ab}^{sat} = 0.33 \mu_B$/f.u. and $M_c^{sat} = 0.36 \mu_B$/f.u. Thus the saturation moment per Co/Ir atom is only about 0.16 and 0.18 $\mu_B$ for these two compositions. The compounds with $x \geq 0.17$ do not show a SF transition. Instead, $M_{ab}(H)$ and $M_c(H)$ almost saturate for $H \gtrsim 3.7$ T.
V. MAGNETISM OF THE GLASSY STATE
FOR 0.17 ≤ x ≤ 0.35

Figure 11 depicts \( \chi_{ab}(T) \) and \( \chi_x(T) \) for \( x = 0.14, 0.17, 0.25, \) and 0.35 measured in \( H = 0.1 \) T, each under both ZFC and FC conditions. The data for the AFM composition \( x = 0.14 \) show no significant hysteresis between the FC and ZFC curves of the respective \( \chi_{ab}(T) \) and \( \chi_x(T) \) measurements. On the other hand, for the compositions \( x = 0.17, 0.25, \) and 0.35, which do exhibit hysteresis, the \( \chi_x \) data for each \( x \) exhibit a broad maximum at a temperature denoting the blocking temperature \( T_B \) as listed in Table II, and \( \chi_{ab} \) shows a FM-like saturation tendency below \( T_B \). The hysteretic behavior of the \( x = 0.17, 0.25, \) and 0.35 compounds of the respective \( \chi_{ab}(T) \) and \( \chi_x(T) \) measurements is similar to the corresponding behavior for different glassy systems consisting of FM clusters [56–60]. In a spin-glass system spin freezing occurs below a blocking temperature \( T_B \) (often called \( T_I \)). Although the measurement of \( T_B \) is best estimated through ac magnetic susceptibility measurements, the \( T_B \) found from that measurement is the same temperature as the temperature of the maximum in the ZFC dc magnetic susceptibility measurement [61,62]. Thus, the data in Fig. 11 for \( x = 0.17, 0.25, \) and 0.35 are consistent with formation of FM clusters in these crystals.

A magnetic glassy state is metastable and found to exhibit a time-dependent relaxation behavior [61,63,64]. Magnetic relaxation dynamics can be studied in different ways. In

TABLE III. Remanent magnetization (\( M_{rem} \)) and coercive field (\( H_{ef} \)) of \( \text{Ca(Co}_{1-x}\text{Ir}_x\text{)}_{2-y}\text{As}_2 \) compounds with \( x = 0.17, 0.25, \) and 0.35.

| Crystal Composition | \( H \) direction | \( M_{rem} \) (\( \mu_B \) f.u.) | \( H_{ef} \) (Oe) |
|---------------------|-----------------|----------------------------|--------------|
| \( \text{Ca(Co}_{0.83}\text{Ir}_{0.17}\text{)}_{1-x}\text{As}_2 \) | \( H \parallel ab \) | 0.019(2) | 220(2) |
|                    | \( H \parallel c \) | 0.012(2) | 190(2) |
| \( \text{Ca(Co}_{0.75}\text{Ir}_{0.25}\text{)}_{1-x}\text{As}_2 \) | \( H \parallel ab \) | 0.038(1) | 87(1) |
|                    | \( H \parallel c \) | 0.018(1) | 88(1) |
| \( \text{Ca(Co}_{0.65}\text{Ir}_{0.35}\text{)}_{1-x}\text{As}_2 \) | \( H \parallel ab \) | 0.047(1) | 90(2) |
|                    | \( H \parallel c \) | 0.019(1) | 92(2) |

FIG. 10. Composition dependence of spin-flop field \( H_{SF} \) and spherically-averaged saturation moment (\( M_{sat,ave} \)) from Fig. 8 for \( \text{Ca(Co}_{1-x}\text{Ir}_x\text{)}_{2-y}\text{As}_2 \) crystals with an A-type AFM ground state. The lines are guides to the eye. According to the extrapolated \( H_{sf}(x) \) data, the A-type AFM phase boundary is at \( x \approx 0.16 \).
FIG. 11. Expanded plots at low temperatures of the magnetic susceptibilities $\chi_{ab}(T)$ and $\chi_{c}(T)$ under ZFC and FC conditions with $H = 0.1 \, \text{T}$ for Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ crystals with compositions $x = 0.14$ to $0.35$. The blocking temperatures $T_B$ for $x = 0.17$, $0.25$, and $0.35$ are indicated by vertical arrows.

In the present work, the crystals were cooled to $2 \, \text{K}$ from $300 \, \text{K}$ in zero applied field by quenching the superconducting magnet in the magnetometer before cooling. After temperature stabilization at $2 \, \text{K}$, a small magnetic field $H = 0.01 \, \text{T}$ was applied and the time $t$-dependent magnetization $M(t)$ was recorded. Figure 12 depicts the magnetic relaxation behavior of Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ crystals with $x \geq 0.14$ measured with $H \parallel ab$ and $H \parallel c$, where the time dependence of the relative change $[M(t) - M(t = 0)]/M(0)$ is presented. As seen from the figure, although little relaxation is apparent for $x = 0.14$, the crystals with $x = 0.17$, $0.25$, and $0.35$ show strong magnetization relaxation for both $ab$-plane and $c$-axis magnetic fields. These results confirm metastable-state formation in the low-$T$ region for $0.17 \leq x \leq 0.35$. The composition $x = 0.14$ is thus close to the boundary between the A-type AFM phase and the FM cluster-glass phase.

We note that the parent compound CaCo$_{2-y}$As$_2$ exhibits A-type AFM ordering with strong magnetic frustration within the $J_1$-$J_2$ Heisenberg model on a square lattice with a nearest-neighbor FM exchange interaction between the Co spins [33].
TABLE IV. Parameters obtained from stretched exponential fits to the magnetic relaxation behavior of Ca(Co_{1−x}Ir_{x})_{2−γ}As_{2} compounds with x = 0.17, 0.25, and 0.35.

| Compound          | H direction | τ (sec) | α  |
|-------------------|-------------|---------|----|
| Ca(Co_{0.83}Ir_{0.17})_{1.87}As_{2} | H || ab    | 3598(107) | 0.44(1) |
|                   | H || c      | 3269(108) | 0.45(1) |
| Ca(Co_{0.75}Ir_{0.25})_{1.80}As_{2} | H || ab    | 3245(87)  | 0.45(1) |
|                   | H || c      | 2909(77)  | 0.45(1) |
| Ca(Co_{0.65}Ir_{0.35})_{1.90}As_{2} | H || ab    | 3840(116) | 0.46(1) |
|                   | H || c      | 3189(106) | 0.42(1) |

Increasing the Ir concentration results in an apparent increase in the FM interaction in these systems. The Ir substitution for Co occurs randomly leading to an increase of the randomly-distributed FM exchange interactions in the crystals. Thus it is plausible that in the presence of frustration and an increase in FM correlations induced by Ir substitution, a low-T magnetically-disordered glassy state is formed for x ≥ 0.17 in Ca(Co_{1−x}Ir_{x})_{2−γ}As_{2}. From Fig. 12, the relaxation is seen to be stronger for the magnetic field aligned in the ab plane compared to the c-axis alignment.

In glassy systems, the relaxation of the magnetization M is often described by a stretched-exponential function with the time t dependence

\[
M(t) / M(t = 0) = 1 - e^{-t/\tau^\alpha},
\]

(7)

where α is the stretched-exponential exponent and τ is a characteristic relaxation time [61,65]. A null value of α signifies no relaxation, whereas α = 1 corresponds to a single magnetization relaxation time. Typically, magnetically disordered glassy systems are characterized by a distribution of energy barriers where the value of α is between 0 and 1.

The time-dependent relaxation of the magnetization of the crystals with x = 0.17, 0.25, and 0.35 toward saturation is indeed well described by Eq. (7), as shown in Fig. 13. The fitted parameters τ and α for each x are listed in Table IV. These results confirm the formation of a magnetically-disordered glassy state in the low-temperature region in Ca(Co_{1−x}Ir_{x})_{2−γ}As_{2} crystals with 0.17 ≤ x ≤ 0.35.

VI. HEAT CAPACITY

Figure 14 shows the zero-field heat capacity C_p(T) of the Ca(Co_{1−x}Ir_{x})_{2−γ}As_{2} crystals in the temperature range 1.8–300 K. The C_p(T) data saturate with increasing T to a value at 300 K close to the classical Dulong-Petit limit C_p = 3nR = 124.7 J/mol K where R is the molar gas constant and here n ≈ 5 is the number of atoms per formula unit.

The low-T C_p(T) data in the temperature range 1.8 K ≤ T ≤ 10 K for the Ca(Co_{1−x}Ir_{x})_{2−γ}As_{2} crystals were analyzed using the relation

\[
C_p(T) = γ T + β T^3 + δ T^5,
\]

(8)

where γ is the Sommerfeld coefficient associated with the itinerant electrons and the last two terms constitute the low-T lattice heat-capacity contribution. The insets in Figs. 14(a)–14(h) show C_p(T)/T as a function of T^2 and the respective fits by Eq. (8). The fitted values of γ, β, and δ are listed in Table V. The γ value increases significantly from 29.6(1) to 48.3(2) mJ mol^−1 K^−2 with only 3.3% Ir substitution for Co in CaCo_{1.86(2)}As_{2}. This result reflects a sharp increase in the density of states at the Fermi energy D(E_F) with Ir substitution as determined from the relationship

\[
D_γ(E_F) \text{(states/eV f.u.)} = \frac{1}{2.357} γ \left( \frac{\text{mJ}}{\text{mol K}^2} \right),
\]

(9)

where this expression for D_γ(E_F) derived from γ includes the factor of two Zeeman degeneracy of the conduction carriers. The values of D_γ(E_F) for the crystals are listed in Table V.

Low-T upturns are observed in the C_p(T) versus T plots in Fig. 16 for the crystals with x = 0.10 and 0.14. The upturn is more pronounced for the latter composition. These upturns are not fitted well by Eq. (8) down to the lowest measured temperature and will therefore be refitted using Eq. (11) below.

TABLE V. The fitting parameters obtained from the analysis of heat-capacity data. The listed parameters are the Sommerfeld coefficient γ, the density of states at the Fermi energy D(E_F) derived from γ using Eq. (9), the lattice heat-capacity coefficients β and δ estimated from the low-T fit of C_p(T) versus T^2 using Eq. (8), and Sommerfeld coefficient γ_0, along with the Debye temperature Θ_D determined by the fit of C_p versus T data using Eqs. (10).

| Compound          | γ  (mJ mol^−1 K^−2) | D(E_F) (states/eV f.u.) | β  (mJ mol^−1 K^−4) | δ  (μJ mol^−1 K^−6) | γ_0 (mJ mol^−1 K^−2) | Θ_D (K) |
|-------------------|---------------------|-------------------------|---------------------|---------------------|----------------------|---------|
| CaCo_{0.86}As_{2} | 29.6(1)             | 12.6(3)                 | 0.391(1)            | ∞0                  | 29.4(3)              | 357(4)  |
| CaCo_{0.967}Ir_{0.033}As_{2} | 48.3(2) | 20.49(8)              | 0.129(8)            | 0.61(6)             | 34(2)                | 344(2)  |
| CaCo_{0.935}Ir_{0.065}As_{2} | 51.6(1) | 21.89(4)              | 0.097(4)            | 0.80(3)             | 35(1)                | 344(2)  |
| CaCo_{0.90}Ir_{0.1}As_{2} | 62.8(1) | 26.64(4)              | 0.025(6)            | 1.26(4)             | 36(1)                | 337(2)  |
| CaCo_{0.86}Ir_{0.14}As_{2} | 61.4(4) | 26.1(2)               | 0.020(10)           | 1.32(7)             | 33(1)                | 331(2)  |
| CaCo_{0.83}Ir_{0.17}As_{2} | 54.4(1) | 23.08(4)              | 0.062(4)            | 0.99(3)             | 31(1)                | 349(2)  |
| CaCo_{0.75}Ir_{0.25}As_{2} | 52.5(8) | 22.3(2)               | 0.060(10)           | 1.11(7)             | 30(2)                | 355(2)  |
| CaCo_{0.65}Ir_{0.35}As_{2} | 47.0(1) | 19.94(4)              | 0.066(5)            | 1.24(3)             | 27(1)                | 349(2)  |
FIG. 14. Temperature $T$ dependence of the heat-capacity $C_p$ for Ca(Co$_{1-x}$Ir$_x$)$_2$As$_2$ crystals in zero field. The red solid lines are fits of the data by the Debye model using Eq. (10). Insets: $C_p/T$ versus $T^2$ in the temperature range $1.8 \, K \leq T \leq 10 \, K$ along with the fits by Eq. (8).

The $C_p(T)$ data were analyzed over the entire temperature range of the measurements using the relation

$$C_p(T) = \gamma_D T + nC_{V\,\text{Debye}}(T),$$

$$C_{V\,\text{Debye}}(T) = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_{\Theta_D}^{T} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$

where $n$ is the number of atoms per formula unit, $\gamma_D$ is the Sommerfeld coefficient derived from the present fit, $C_{V\,\text{Debye}}$ is the Debye lattice heat capacity per mole of atoms at constant volume, and $\Theta_D$ is the Debye temperature. The fitted values of $\gamma_D$ and $\Theta_D$ for all the crystals are listed in Table V. The values
of $\gamma$ and $\gamma_D$ are the same for the parent compound with $x = 0$ but differ significantly from each other for the Ir-substituted crystals with $x > 0$ as shown in Table V and Fig. 15, where $\gamma_D \sim \gamma/2$.

To investigate the origin of the low-$T$ upturns in $C_p(T)/T$ versus $T$ for the Ca(Co$_{1-x}$Ir$_x$)$_{2-y}$As$_2$ crystals with $x = 0.10$ and 0.14 in Fig. 16, the dependence of $C_p(T)$ on applied $c$-axis fields from 0 to 7 T was measured for $x = 0.10$ and 0.14 together with analogous measurements of the neighboring compositions $x = 0.065$ and 0.17. Figure 16 shows that the magnetic field strongly alters $C_p(T)/T$ versus $T$ for $x = 1.4$, moderately alters those of the crystals with $x = 0.10$ and 0.17, and has almost no influence for $x = 0.065$. The low-$T$ upturn for $x = 0.14$ is strongly suppressed by the applied field. Such types of behavior have been previously observed for different compounds with FM quantum-critical fluctuations [66,67] and were also recently reported to occur in isostructural Sr(Co$_{1-x}$Ni$_x$)$_2$As$_2$ crystals [37].

In this context, we recall that with increasing Ir substitution for Co in CaCo$_{1.86}$As$_2$, FM interactions increase significantly and FM clustering occurs for $x \geq 0.17$. Furthermore, the above analyses revealed that the $x = 0.14$ composition is close to the phase boundary between the competing A-type AFM phase and magnetically-disordered FM cluster-glass phase. Thus, it seems reasonable to interpret the upturn in $C_p(T)/T$ at low $T$ for $x = 0.14$ as arising from FM quantum-critical fluctuations associated with a quantum-critical composition between the AFM and FM cluster-glass states.

In some systems, a $C_p(T)/T \sim \ln T$ contribution attributed to quantum-critical fluctuations has been included to fit the low-$T$ $C_p(T)$ data in addition to electronic and lattice heat-capacity contributions [37,68,69]. Therefore, for our crystals with $x = 0.10$ and 0.14, we analyzed the $C_p(T)/T$ versus $T$ data using the relation

$$\frac{C_p(T)}{T} = \gamma_{SF} + \beta_{SF}T^2 + \delta_{SF}T^4 + \kappa\ln(T/T_{SF}).$$  \hspace{1cm} (11)

where $\gamma_{SF}$ is the Sommerfeld coefficient determined from this fit, $\beta_{SF}$ and $\delta_{SF}$ are the lattice heat-capacity coefficients from this fit, $\kappa$ is the spin fluctuation coefficient, and $T_{SF}$ is the spin fluctuation temperature. The low-$T$ upturns seen in the data for the $x = 0.10$ and 0.14 crystals are well fitted by incorporating the latter term, as shown in Fig. 17. The fitted parameters are listed in Table VI.
An approximate phase diagram in the temperature-composition plane of the Ca(\(\text{Co}_{1-x}\text{Ir}_x\))\(_{2-y}\text{As}_2\) system is shown in Fig. 18 based on the presently-available \(T_N(x)\) and \(T_B(x)\) data. Also included is the concentration dependence of the spin-flop field \(H_{SF}\) which is expected to be correlated with \(T_N\) and is therefore used to help delineate the boundaries between the AFM, PM, and FMCG phases.

### VII. SUMMARY

In this paper, we investigated the physical properties of Ir-substituted Ca(\(\text{Co}_{1-x}\text{Ir}_x\))\(_{2-y}\text{As}_2\) single crystals with 0 \(\leq x \leq 0.35\) and 0.10 \(\leq y \leq 0.14\) that were grown out of Co-Ir-As self flux. Room-temperature x-ray diffraction measurements showed that all the crystals form in the collapsed-tetragonal structure, as does the parent compound CaCo\(_{2-y}\text{As}_2\). The SEM-EDS results showed that the vacancy concentration on the Co site is sensitive to the Ir concentration \(x\), which changes from 7\% in the parent CaCo\(_{2-y}\text{As}_2\) to 5\% in the 35\% Ir-substituted composition. Both the tetragonal lattice parameters \(a = b\) and \(c\) were found to increase nonlinearly with \(x\), yielding a nonlinear unit cell volume versus \(x\).

The temperature dependence of the static magnetic susceptibility \(\chi\) shows that the A-type AFM transition temperature \(T_N = 52\) K of CaCo\(_{2-y}\text{As}_2\) rapidly drops to 23 K with only 3.3\% Ir substitution. Increasing \(x\) dramatically enhances ferromagnetic fluctuations, both in plane and out of plane, and further decreases \(T_N\) which approaches zero for \(x = 0.14\). A phase transition then occurs at \(x \approx 0.16\) to a ferromagnetic cluster-glass phase for 0.17 \(\leq x \leq 0.35\) below a blocking temperature \(T_B \leq 5\) K, exemplified by observations of magnetization irreversibility between zero-field-cooled and field-cooled measurements, a small spontaneous ferromagnetic component to the ordering, and spin-glass-type stretched-exponential dynamics in the time dependence of the magnetization response to a small applied field.

The zero-field heat-capacity \(C_p(T)\) reveals a strong increase in the Sommerfeld heat-capacity coefficient \(\gamma\) with Ir substitution, signifying a corresponding increase in the electronic density of states at the Fermi energy in the Ir-substituted Ca(\(\text{Co}_{1-x}\text{Ir}_x\))\(_{2-y}\text{As}_2\) crystals. A low-temperature upturn in \(C_p/T\) versus \(T\) is observed for \(x = 0.10\) and 0.14, with the strongest such contribution for \(x = 0.14\), near the boundary between the A-type AFM phase and the FMCG phase. The upturn in \(C_p/T\) versus \(T\) for \(x = 0.14\) is fitted well by a logarithmic temperature dependence that we associate with ferromagnetic quantum-critical spin fluctuations. The observed upturn in \(C_p/T\) versus \(T\) is strongly suppressed by an \(H = 7\) T magnetic field, consistent with this interpretation.

Thus, increasing the random Ir-substitution for Co in CaCo\(_{2-y}\text{As}_2\) results in a strong increase in FM interactions that in turn results in a phase transition at \(x \approx 0.16\) from A-type AFM to a FMCG phase. The composition \(x = 0.14\) which is close to the transition composition exhibits a signature of ferromagnetic quantum fluctuations. We infer that the FMCG phase at larger \(x\) (\(x = 0.17, 0.25, 0.35\)) arises from a competition between AFM and FM interactions in conjunction with crystallographic disorder accompanying Ir substitution. The properties of the Ir-substituted Ca(\(\text{Co}_{1-x}\text{Ir}_x\))\(_{2-y}\text{As}_2\) system are distinctly different from the behavior seen previously in other doped ACo\(_2\text{As}_2\) systems. It would be interesting to study theoretically the influence of the 5\(d\) orbitals and spin-orbit coupling associated with the Ir atoms on the results presented in this paper.

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