Incommensurate magnetism near quantum criticality in CeNiAsO

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We report the discovery of incommensurate magnetism near quantum criticality in CeNiAsO through neutron scattering and zero field muon spin rotation. For $T < T_{N1} = 8.7(3)$ K, a second order phase transition yields an incommensurate spin density wave with wave vector $k = (0.44(4), 0.0)$. For $T < T_{N2} = 7.6(3)$ K, we find co-planar commensurate order with a moment of $0.37(5) \mu_B$, reduced to 30 % of the saturation moment of the $|\pm \frac{1}{2}\rangle$ Kramers doublet ground state, which we establish through inelastic neutron scattering. Muon spin rotation in CeNiAs$_{1-x}$P$_x$O shows the commensurate order only exists for $x \leq 0.1$ so we infer the transition at $x_c = 0.4(1)$ is between an incommensurate longitudinal spin density wave and a paramagnetic Fermi liquid.

The competing effects of intra-site Kondo screening and inter-site Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions in rare earth intermetallics epitomize the strongly correlated electron problem. While the Néel and Kondo lattice limits are well understood [1], the transition between them is far from. It involves an increase in the volume enclosed by the Fermi surface (FS) as the $4f$ electron is incorporated on the Kondo lattice side of the transition [2, 3]. Deviations from the $\rho \propto T^2$ dependence of resistivity is interpreted as indicative of the associated quantum criticality, which is denoted as “local” because it involves the entire FS. In support of this concept, compounds with the requisite transport anomalies have been discovered where physical properties that involve averages over distinct regions of momentum space have related critical exponents. The eventual transition to magnetic order when RKKY interactions dominate can coincide with the localization transition or occur within the large or small FS phases. Clearly the nature of the corresponding quantum critical point is strongly affected as magnetic ordering is momentum selective and breaks time reversal symmetry.

Exploration of model systems is essential to uncover the overall phase diagram of this complex strongly correlated regime. CeCu$_{6-x}$Au$_x$ provided a first example of local criticality. de Haas-van Alpen measurements provide evidence for an abrupt rearrangement of the FS in CeRhIn$_5$ at 2.25 GPa [4–6]. A step change in the Hall coefficient of YbRh$_2$Si$_2$ coupled with anomalous and yet unexplained critical exponents at the field driven ferromagnetic transition have been interpreted as evidence the magnetic and the electron localization transitions coincide [7–11]. Each compound adds unique insights and distinct experimental opportunities.

Isostructural to the 1111 iron pnictides, CeNiAsO is an exciting new addition to the landscape of strongly correlated electron systems [12]. Magnetically ordered at low $-T$ and ambient pressure, substitution of P for As or pressure drives CeNiAs$_{1-x}$P$_x$O to a paramagnetic Fermi-liquid. Non-Fermi-liquid transport is found up to the critical pressure $P_c = 6.5$ kbar and the critical composition $x_c = 0.4(1)$ and a sign change in the Hall coefficient at $P_c$ indicates FS reconstruction [13]. CeNiAsO differs from other systems studied to date in having two magnetic phase transitions [12].

In this letter we determine the corresponding magnetic phases and examine their interplay with FS reconstruction. We show the upper transition is to an incommensurate longitudinal SDW state with wave vector $k = (0.44(4), 0.0)$ that closely matches the umklapp wave vector $(2k_f)$ of the small FS. The second transition yields co-planar commensurate order with a low $-T$ ordered moment reduced to 30% of the saturation moment of the nominal $|\pm \frac{1}{2}\rangle$ Kramers doublet ground state. P doping suppresses the commensurate phase but retains the SDW perhaps all the way to the critical
FIG. 1: (a) Crystallographic structure of CeNiAsO, and spin structure for $T_{N2} < T < T_{N1}$ (b) and $T < T_{N2}$ (c). Blue stars indicate the single crystallographic muon site. Two equivalent muon sites above and below oxygen site become inequivalent within the magnetically ordered state. (d) Temperature-doping phase diagram. Red, blue, and green symbols are from specific heat, $\mu$SR, and neutron data respectively. Brown dots are from Luo et al. [13]. We assign open (closed) symbols to the higher (lower) $T$ transition. The inset to (d) shows the $q_z = 0$ small Fermi surface excluding 4$f$ electrons. The arrow shows the magnetic wave vector, which connects extended areas of the Fermi surface. The dashed lines are guides to the eye.

concentration where the FS grows to include 4$f$ electrons.

We probed the magnetism of CeNiAsO through magnetic neutron scattering on the NOMAD and POWGEN diffractometers [14, 15] and on the SEQUOIA [16] spectrometer at the Spallation Neutron Source. For complementary real space information we used muon spin rotation ($\mu$SR) at the M15 beam line at TRIUMF. Specific heat measurements were conducted on a 14 Tesla Quantum Design PPMS with a dilution fridge insert.

Fig. 1(a) shows the tetragonal structure of CeNiAsO where magnetism is associated with Ce$^{3+}$ sandwiching a square lattice of oxygen. The structure and the single phase nature of the sample was ascertained by Rietveld refinement of high resolution neutron diffraction data (see SI). The specific heat data in Fig. 3(d) show shoulder-like anomalies indicating two second order phase transitions at $T_{N1} = 9.0(3)$ K and $T_{N2} = 7.6(3)$ K. The inferred critical temperatures are consistent with previously published specific heat data with sharper peaks indicating higher purity[12]. The rounded maxima shift towards lower $T$ and approach each other in a field of $\mu_0 H = 14$ T as for two distinct antiferromagnetic phases.

To determine their nature, we use zero field $\mu$SR in the longitudinal configuration [17, 18]. Fig. 2 shows muon spin precession indicative of a well defined static internal field for $T < T_{N1}$. A qualitative change in the $\mu$SR profile for $T < T_{N2}$ indicates two distinct magnetic phases. For $T_{N2} < T < T_{N1}$, muons sample the broad spectrum of local fields generated by an incommensurate SDW [19]. For $T < 6$ K, the signal is oscillatory (Fig. 2 (b)) with a beating pattern that indicates two distinct precession frequencies and commensurate magnetism. These patterns can be fitted by magnetic structures that are consistent with the neutron data and a single crystallographic muon stopping site.

We determined the fundamental magnetic wave vector and spin polarization through neutron diffraction. Weak magnetic peaks are apparent at $T = 2$ and 8 K after subtracting data at $T = 15$ K (Fig. 2 (c-d)). At $T = 2$ K, the difference pattern shows several resolution limited peaks. The peak with the lowest wave vector transfer $Q \approx 0.77 \text{Å}^{-1}$ can be indexed as $Q_m = (0.5, 0, 0)$. Magnetic neutron diffraction probes spin polarization perpendicular to wave vector transfer so this indexing implies spin components along b and/or c. Upon warming to 8 K < $T_{N1}$, the absence of this first peak is indicative of a longitudinal spin density wave (SDW) polarized along a. The width of the intensity maxima for $T = 8$ K and $Q \approx 1.1 \text{Å}^{-1}$ in Fig. 2 (c) exceeds the instrumental $Q$-resolutions. The incommensurability indicated by $\mu$SR can account for this. The magnetic signal at 8 K is however quite weak and since there is no energy resolution, inelastic magnetic scattering may also contribute to the broadened peaks, particularly near the polarization suppressed $Q_m$ peak. The diffraction data thus do not permit a unique determination of the spin structure for $T_{N2} < T < T_{N1}$. The combination of muon, specific heat, and elastic/inelastic neutron data, however, does allow an accurate determination of both structures.

Using Kovalev notation [20, 21], the reducible magnetic representation associated with $k = (\mu 00)$ decomposes into three two-dimensional irreducible representations (IR): $\Gamma_{mag} = 2\Gamma_1^{(2)} + \Gamma_2^{(2)}$ with 6 Basis Vectors (BVs) (Table S2). Landau theory allows only one IR for each of the two second order phase transitions. Below $T_{N1}$, BVs $\psi(4)$ and $\psi(6)$ of $\Gamma_1$ depict a spin structure with
moments along $\mathbf{a}$. Adding $\psi(3)$ and $\psi(5)$ allows for moments along $\mathbf{c}$. Below $T_{N2}$, we can account for the precession pattern in Fig. 2 (d) by adding $\psi(1)$ and $\psi(2)$ to $\Gamma_2$. The best fit corresponds to a reduced $\chi^2 = 1.95$ and a staggered moment $\langle m \rangle = 0.37(5) \mu_B/\text{Ce}$ that is canted by $\varphi \approx 36(6)^\circ$ to the $a$ axis (Fig. 1 (c)). While allowed by symmetry, the precession data place a limit of 0.06 $\mu_B$ on any $c$-component of the staggered moment.

$\mu$SR, which probes magnetism in real space, offers an independent assessment of the proposed structures. We find a consistent description of the precession data with the muon stopping site $(\frac{1}{4}, \frac{1}{4}, z_\mu)$ in Fig.1 (a). The fitting analysis described below yields $z_\mu = 0.1471(3)$ ($\approx z_{\text{Ce}}$), close to the preferred distance of muons from O$^{2-}$ [22]. This location is also favored considering the electrostatic potential-energy map for CeFeAsO [23]. The observation of two muon precession frequencies suggests two magnetically inequivalent muon sites (see Fig.1 (b-c)). The asymmetry pattern $P^\mu_1(t)$ can be fitted to equation S1 therein the magnetic field distribution function $\rho_1(B)$ is calculated directly from the spin structures. For the low $T$ commensurate state, $\rho_1(B)$ consists of two delta functions corresponding to the magnetic field at each of the two magnetically inequivalent (but crystallographically equivalent) muon sites. The best fit is obtained with moment $m = 0.37(2) \mu_B$ and rotation angle $\varphi = 36(7)^\circ$, which is in excellent agreement with the Rietveld refinement of neutron diffraction. For the high $T$ incommensurate state, $\rho_1(B)$ is continuous: The incommensurate nature of the spin structure ensures every muon site, though crystallographically equivalent, is magnetically unique and contributes a distinct precession frequency. The best fit leads to an incommensurate wave vector $k = (0.44(4), 0, 0)$, $m_a = 0.27(6) \mu_B$, and $m_c = 0.08(3) \mu_B$. The corresponding calculated muon asymmetry and neutron diffraction are in Fig. 2 (a) $k(c)$. A small component of $m_c$ implies this is a magnetic cycloid. The corresponding lack of inversion symmetry could have interesting consequences for electronic transport. However, since $m_c \ll m_a$ we retain the terminology of a longitudinal SDW. In summary, the spin structures for two ordered states – a longitudinal SDW (Fig. 1 (b), Fig. S4) and a commensurate coplanar structure (Fig. 1 (c)) – account for both neutron and $\mu$SR data.

For context we examine the 4$f$ electron crystal field excitations through inelastic magnetic neutron scattering (Fig. 4 (a-c)). At $T = 7$ K, the intensities of modes at $E \approx 10$ meV, 30 meV and 40 meV rise with $Q^2$ and are observed both for CeNiAsO and non-magnetic LaNiAsO and so must be vibrational [27]. In the difference data $\tilde{I}(Q, E)$ and $\tilde{I}(E)$ (Fig. 4 (c-e)), we associate the two broad modes at $E_1 \approx 18(3)$ meV and $E_2 \approx 70(8)$ meV with magnetic excitations because their intensity decreases with $Q$ as the 4$f$ formfactor. In the tetragonal environment of Ce$^{3+}$, the $J = \frac{5}{2}$ multiplet splits into three Kramer’s doublets. The two magnetic modes are correspondingly assigned to crystal-field-like excitations from the ground state (GS) to two excited doublets. At $T = 200$ K population of the excited state yields a broad mode at $50$ meV to $E_2 - E_1$, which arises from excitations between the excited doublets. Finally we observe a sharp mode at $E_0 \approx 2$ meV within the AFM ordered state (inset, Fig.4 (d)). In the language of CEF theory, this is an intra-doublet transition driven to inelasticity by the molecular exchange field. As expected for a strongly correlated solid, the crystal field excitations measured for a powder sample are broadened by damping and...
The ordering wave vector $\mathbf{k} = (0.44(4), 0, 0)$ satisfies a nesting condition. This suggests the ordered state for $T_{N2} < T < T_{N1}$ should be classified as a SDW [28–32]. It is common for incommensurate (IC) magnets to undergo a longitudinal to transverse spin reorientation transition that reduces the modulation in the magnitude of the dipole moment per unit cell while sustaining the IC modulation [30, 33]. The situation is different for CeNiAsO, which not only develops transverse magnetization but also becomes commensurate for $T < T_{N2}$. To arrive at the spin structure in Fig. 1 (c) from the commensurate version of Fig. 1 (b) involves counter-rotating the upper and lower AFM layers of a CeO sandwich (Fig. 1 (a)) by $\varphi = 36^\circ(5)$ around c. While inter-layer bi-linear interactions vanish at the mean field level for $\mathbf{k} = (0.5, 0, 0)$ type order, inter-layer bi-quadratic interactions[34, 35] give rise to a term in the free energy of the form $(m^2 \cos 2\varphi)^2$ that can favor $\varphi = 45^\circ$ for a commensurate structure only. As $m$ grows upon cooling this term can be expected to induce both the IC to commensurate transition and the symmetry breaking transverse magnetization at $T_{N2}$.

This brings us to the character of magnetism in CeNiAs$_{1-x}$P$_x$O. Upon cooling, CeNiAsO passes from Fermi liquid to IC SDW to commensurate non-collinear order in two second order phase transitions. P doped samples that we examined (CeNiAs$_{1-x}$P$_x$O for $x > 0.1$)
all show the characteristic µSR oscillation associated with IC magnetism (Fig.2 (a)) down to 50 mK. This indicates the commensurate state is limited to a low T, low x pocket (Fig. 1 (d)) and the initial instability of the strongly correlated Fermi liquid in CeNiAs$_1-x$PxO is to an IC SDW. An important open question is whether the characteristic wave vector of the SDW evolves with $x$ or continues to be associated with the small FS as for $x = 0$.

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Synthesis method

Samples of CeNiAsO were synthesized by pelletizing CeO$_2$ (Alfa Aesar, 99.99 %), NiAs (pre-fired), and Ce metal (Alfa Aesar, 99.8 %) stoichiometrically, sealing the pellet in an evacuated-fused silica tube. The reaction ampoule was placed in a furnace and heated to 1000 °C at a rate of 100 °C/hr. The temperature was held constant at 1000 °C for 5 hours. The ampoule was then allowed to furnace cool to room temperature.

Phosphorous doped samples were synthesized following the procedure described in Ref. [1]. For each sample, CeO$_2$, Ni$_5$P$_4$ (pre-fired), Ce metal, purified and dried P, and NiAs (pre-fired) were mixed and ground thoroughly and stoichiometrically to CeNiAs$_{1-x}$P$_x$O$_{0.98}$. The pressed pellet was placed in a dry alumina crucible and sealed into an evacuated ampoule. The ampoule was heated from 750 °C to 1050 °C over 1 hour and held at 1050 °C for 5 hours. After cooling to room temperature in the furnace, the sample was re-grounded and re-pressed with excess of 2 % P to account for vaporization during pre-reaction. The sample was then pressed into a pellet again and placed in the same alumina crucible into a new ampoule. The ampoule was heated from 750 °C to 1050 °C over 1 hour and held at 1050 °C for 5 hours. After cooling to room temperature in the furnace, the sample was re-grounded and re-pressed with excess of 2 % P to account for vaporization during pre-reaction. The sample was then pressed into a pellet again and placed in the same alumina crucible into a new ampoule. The ampoule was sealed into a larger ampoule backfilled with 1/3 atm Ar (99.99%). This ampoule was placed directly into a furnace that was pre-heated to 1300 °C and it remained there for 8-12 hours. After cooling on the bench top, such heating to 1300 °C and bench-top cooling was repeated 2-4 times with intermediate grinding, until the starting materials were no longer visible in powder x-ray diffraction (details later). The entire synthesis was conducted in an argon atmosphere. The sample was exposed to air less than 10 mins during each regrind/reheat/reseal cycle.

Nuclear structure determination

The structure of CeNiAsO was determined by Rietveld refinement of T = 300 K data acquired on POWGEN (Fig. S1), using Fullprof[2]. The data were refined in the tetragonal space group P4/nmm. The corresponding atomic positions and lattice parameters are listed in Table S1 (Bragg R-factor = 5.37). The inferred structure is consistent with powder x-ray diffraction (XRD) refinement. Laboratory powder x-ray diffraction data were collected using a Bruker D8 Focus diffractometer equipped with Cu Kα radiation and a LynxEye detector. Phase identification and phase purity checks were conducted through Rietveld refinement. A 4 hours XRD measurement found only 0.75% by volume of CeNi$_2$As$_2$ as the only detectable impurity phase. A pair distribution analysis of the NOMAD data found no evidence of a local structural distortion as in CeFeAsO [3].
TABLE S1: $T = 300$ K atomic positions for CeNiAsO with space group $P4/nmm$ determined by the Rietveld refinement of neutron powder diffraction data. The corresponding lattice parameters are $a = 4.0621(1)$ Å and $c = 8.1058(3)$ Å.

| Atom | Site | $x$  | $y$  | $z$  | $U_{iso}$(Å$^2$) |
|------|------|------|------|------|-----------------|
| Ce   | 2c   | 1/4  | 1/4  | 0.1471(3) | 0.0070(5) |
| Ni   | 2b   | 3/4  | 1/4  | 1/2   | 0.0120(3)     |
| As   | 2c   | 1/4  | 1/4  | 0.6439(3) | 0.0081(4) |
| O    | 2a   | 3/4  | 1/4  | 0     | 0.0056(4)     |

$R_{wp} = 7.07$, $R_p = 10.3, R_{exp} = 2.06, \chi^2 = 10.9$

TABLE S2: The 6 basis vectors associated with magnetic structures that transform according to irreducible representations with propagation vector $k = (1, 0, 0)$, using Kovalev notation as implemented in SARAh.

| IR   | BV  | Atom1  | Atom2  |
|------|-----|--------|--------|
| $\Gamma_2$ | | $m_x m_y m_z$ | $m_x m_y m_z$ |
| $\psi(1)$ | 0 0 0 | 0 -1 0 |
| $\psi(2)$ | 0 1 0 | 0 0 0 |
| $\psi(3)$ | 0 0 1 | 0 0 0 |
| $\psi(4)$ | 0 0 0 | 1 0 0 |
| $\psi(5)$ | 0 0 0 | 0 0 1 |
| $\psi(6)$ | 0 0 0 | 0 0 0 |

CeNiAs$_{1-x}$P$_x$O samples with nominal values of $x=0.2$, 0.3, 0.4, and 0.5, we found $x = 0.19(1)$, 0.29(1), 0.33(1) and 0.49(1) respectively. These values were consistent with SEM/EDX measurements.

EXPERIMENTAL DETAILS

Elastic scattering

Neutron diffraction was carried out using the Nanoscale Ordered Materials Diffractometer (NOMAD) at the Oak Ridge National Laboratories (ORNL). Data were collected with a total proton charge of 4.5 mAh at $T = 2$ K, 8 K, and 15 K, with a 30 Hz bandwidth (BW) chopper, admitting a wavelength band from 0.1 Å to 3 Å in the first frame. Temperature dependence measurements were obtained with a proton charge of 2 mAh each from 2 K to 10 K in 2 K steps, with 60 Hz pulse rate admitting a wavelength band from 3 Å to 6 Å. We used a vanadium sample can and corrected for background through separate measurements of the empty instrument and an empty sample can. Diamond scans were used for calibration purposes. Absolute units for magnetic diffraction were obtained by scaling to nuclear Bragg intensities.

Inelastic scattering

Inelastic neutron scattering was performed using the SEQUOIA Fermi chopper spectrometer at SNS, ORNL.

$\mu$SR experiment

We performed zero field (ZF) $\mu$SR with the detectors in the longitudinal configuration on the M15 beam line at Canada’s national laboratory for particle and nuclear physics (TRIUMF). The samples were mounted using Apiezon N grease, covered with Alfa Aesar 0.025 mm thick silver foil, and cooled in a dilution refrigerator to 0.04 K.

The asymmetry pattern $P^z_\mu(t)$ can be fitted to the following expression:

$$A_s \sum \left( \frac{2}{3} e^{-\lambda_i t} \int \rho_i(B) \cos(\gamma_i B t) dB + \frac{1}{3} e^{-\lambda_i t} \right) + A_{bg} e^{-\lambda_{bg} t}$$

(S1)

Here $A_s$ is the total asymmetry stopped in the sample at $t = 0$. We assume equal weight for the two magnetically distinct muon sites (ratio = 1.0(2)). $\rho_i(B)$ is the magnetic field distribution at the muon site $i$. $\lambda_i$ and $\lambda_{bg}$ are the rapid transverse and slow longitudinal rate respectively, and $\gamma_i / 2\pi = 135.53$ MHz $T^{-1}$ is the gyromagnetic ratio of the muon. The last term accounts for muons stopped beyond the sample.

We calculated the internal field distribution $\rho_i(B)$ on the putative muon interstitial sites and spin configurations for comparison to the $\mu$SR data. For
calculating the local magnetic field on one muon site we summed contributions from 61 crystallographic unit cells. This is sufficient to reach convergence of the internal field. For the low-\(T\) commensurate phase, plugging the value of field into Eq. S1 and comparing to the oscillation pattern, we determined the moment \(m\) and the rotation angle \(\phi\) (Fig. S2). The transverse and longitudinal moment \(m_{\parallel}\) \((m \cot \phi)\) and \(m_{\perp}\) \((m \tan \phi)\) was also inferred and plotted in Fig. 3 (a-b). For the high-\(T\) phase, the frequency density is shown in Fig. S3. We performed an average over the phase of the incommensurate spin configuration (Fig. S4). From the optimal fits to \(T = 7\) K \(\mu\)SR data, we determined the wave vector \(k\), the moment amplitude along the \(a\)-axis and the \(c\)-axis, \(m_a\) and \(m_c\) respectively. Throughout the measured temperature range, the \(T\)-dependence of \(m_{\parallel}\) and \(m_{\perp}\) obtained from the \(\mu\)SR analysis are consistent with the values obtained from Rietveld refinement of neutron powder diffraction.

![FIG. S4: Longitudinal incommensurate magnetic structure in CeNiAsO. Also shown is a small transverse component along the \(c\)-axis that is allowed by symmetry and improves the Rietveld fit to the magnetic neutron powder diffraction data.](image)

**LOW TEMPERATURE SPECIFIC HEAT ANOMALY**

Specific heat data were acquired using a quantum design Physical Properties Measurement System with a dilution refrigerator insert for measurements below 2 K. The single pulse method was employed near the ordering temperature and otherwise we used the adiabatic method. Two successive anomalies \(T_{N1} = 9.3(3)\) K and \(T_{N2} = 7.6(3)\) K were observed in the specific heat data as studied and discussed in the main text. The error bar for the two characteristic temperatures were estimated. A strong upturn in \(C_p / T\) below 0.1 K (Fig. S5 (a) ) is identified as a hyperfine enhanced \(^{61}\)Ni nuclear Schottky anomaly. It can be accounted for by the following expression[7, 8].

\[
C_N = E_N^{2} \beta^{2} R \frac{e^{-E_N \beta}(1 + e^{-E_N \beta})^{4} + 4e^{-3E_N \beta}}{(1 + e^{-E_N \beta} + e^{-2E_N \beta} + e^{-3E_N \beta})^{2}}
\]

Here \(E_N = -g_N \mu_N \Delta IB\) is the level splitting, where \(\mu_N\) is nuclear magneton and \(g_N\) is the nuclear gyromagnetic ratio. The inset in Fig. ?? (d) shows a broad specific heat anomaly at \(T_3 = 0.5\) K after subtracting the nuclear Schottky anomaly.

The corresponding change in entropy, \(S(\mu_0 H = 14\) T)-\(S(\mu_0 H = 0\) T) \(\approx 80\) mJ/K/mol/f.u. up to 2.2 K, is 1.4\% of a full doublet entropy \(R \ln 2\). Resistivity measurements on a polycrystalline sample show no indication of a superconducting phase transition down to 55 mK. In addition, no clear change of oscillation patterns were observed in \(\mu\)SR spectra (Fig. S5 (b)). Possible explanations for the low \(T\) specific heat anomaly are (1) coherence effects in the Kondo lattice as for CeAl\(_3\) [9], (2) changes in the magnetic domain wall configuration and (3) partially gapped Fermi surface with approximation (L(S)DA). An 11x11x11 gamma-centered Monkhurst-Pack k-point grid was used for all calculations along with an upper energy cut-off 434 eV, and a convergence of the total energy to better than 0.01\%. The calculations proceeded in three steps. First, a structural and ionic relaxation was performed, with the ionic relaxation considered complete when the total free energy difference between steps was less than 0.1 \%. Second, a non-magnetic static calculation using this structure was performed. Finally, a magnetic static calculation initiated from the converged (non-magnetic) charge density was performed. For the magnetic calculation, an initial 0.5 \(\mu_B\) magnetic moment along \(\pm c\) was applied to the Ce sites, converging to a simplified anti-ferromagnetic structure with a moment of 0.1 \(\mu_B\) per Ce. Spin-orbit interactions and an onsite (Ce) Hubbard \(U\) of 7.5 eV with an exchange \((J)\) parameter of 0.68 eV were included in all calculations.

**DFT calculation**

Electronic structure calculations were conducted using the Vienna Ab-Initio Simulation Package (VASP), which models valence electrons using projector augmented plane waves (PAW) [4–6]. The exchange-correlation effects were modeled using the local (spin) density approximation (L(S)DA).
FIG. S5: CeNiAsO: (a) specific heat data acquired in a PPMS plotted as $C_p/T$ for temperatures below 2 K, after subtracting the calculated hyperfine nuclear spin contributions for zero field and 15 T. (b) Extracted average field below 1 K from muon spin rotation measurement.

sensitivity to an applied fields (4) an anomaly associated with a second phase in the sample.

CRYSTAL FIELD ANALYSIS

The crystal field inelastic spectrum (Fig. ?? (c)-(e)) was obtained from inelastic neutron scattering data acquired on SEQUOIA after subtracting scaled data from the non-magnetic reference sample LaNiAsO and normalizing based on Bragg diffraction. In the PM phase the Hamiltonian is expressed in terms of Stevens operators [30] that are allowed by the point group symmetry and account for the observed CEF modes. In the ordered state, a mean field description of inter-site interactions adds a molecular field term. The inelastic neutron scattering cross section acquired with incident energy $E_i = 50$ meV in Fig. 4. (d-e) is obtained from state $|i\rangle$ to $|j\rangle$ can be expressed as follows [11]:

\[
\frac{d^2\sigma}{d^2d\omega} = N\frac{k_f}{k_i} \frac{1}{2} g_j r_0 F(Q)|^2 \times \sum_{i,j} p_i|\langle i|J_{\alpha}|j\rangle|^2 \delta(E_i - E_j + \hbar\omega) \tag{55}
\]

We replaced the Dirac delta function with a unity normalized Lorentzian function with Half Width at Half Maximum (HWHM) $\Gamma_n = 13(2), 23(3), 24(1)$ meV for the three CEF modes and $\Gamma_0 = 2.0(2)$ meV for the sharp low energy mode. The width of three modes are much broader than the instrumental resolution even under the $E_i = 50$ meV configuration. The dispersive bands of hybridized $4f$ and conduction electrons may account for the broadening. The molecular field term $B_{\text{eff}} \cdot J$ can be further simplified as $B_{\text{eff}} J_{\parallel}$, considering an in-plane effective field. Three CEF parameters and one molecular field parameter were obtained by fitting to the $T$-dependent magnetic neutron scattering spectra. The corresponding fitting parameters and wave functions are listed in Table S3 - S5 for the PM and ordered states. The schematic crystal field scheme is displayed in Fig. S7. The difference in $B^0_2$ and $B^1_4$ between the two measurements is within error bars. The sign change for $B^1_4$ could result from a multipolar mean field.

The cross section for unpolarized neutron scattering from a polycrystalline sample arising from transitions from state $|i\rangle$ to $|j\rangle$ can be expressed as follows [11]:

\[
\frac{d^2\sigma}{d^2d\omega} = N\frac{k_f}{k_i} \frac{1}{2} g_j r_0 F(Q)|^2 \times \sum_{i,j} p_i|\langle i|J_{\alpha}|j\rangle|^2 \delta(E_i - E_j + \hbar\omega) \tag{55}
\]

We replaced the Dirac delta function with a unity normalized Lorentzian function with Half Width at Half Maximum (HWHM) $\Gamma_n = 13(2), 23(3), 24(1)$ meV for the three CEF modes and $\Gamma_0 = 2.0(2)$ meV for the sharp low energy mode. The width of three modes are much broader than the instrumental resolution even under the $E_i = 50$ meV configuration. The dispersive bands of hybridized $4f$ and conduction electrons may account for the broadening. The molecular field term $B_{\text{eff}} \cdot J$ can be further simplified as $B_{\text{eff}} J_{\parallel}$, considering an in-plane effective field. Three CEF parameters and one molecular field parameter were obtained by fitting to the $T$-dependent magnetic neutron scattering spectra. The corresponding fitting parameters and wave functions are listed in Table S3 - S5 for the PM and ordered states. The schematic crystal field scheme is displayed in Fig. S7. The difference in $B^0_2$ and $B^1_4$ between the two measurements is within error bars. The sign change for $B^1_4$ could result from a multipolar mean field.

| $T$ (K) | $B^0_2$ (meV) | $B^1_4$ (meV) | $B^2_4$ (meV) | $B_{\text{eff}}$ (T) |
|--------|-------------|-------------|-------------|-----------------|
| 7      | 3.1(1)      | 0.07(1)     | 1.1(1)      | 1.7(2)          |
| 200    | 2.3(1)      | -0.09(4)    | 0.9(1)      | -               |

To verify the scheme of crystal field, we also measured the magnetic susceptibility of a polycrystalline sample. The data was collected with external field $H = 1000$ Oe as shown in Fig. S8. The magnetic susceptibility $\chi_\alpha$
TABLE S4: Wave functions considering the effective molecular field at $T = 7$ K. The three doublets are divided into 6 non-degenerate singlets. The $\pm$ sign prior to the coefficient indicates summation over each component of angular moment.

| Energy (meV) | Doublet wave function |
|-------------|----------------------|
| $\psi_5$    | $|\pm 0.641\pm 0.298\pm 0.009\pm \frac{1}{2}|$ |
| $\psi_4$    | $|\pm 0.648\pm 0.281\pm 0.008\pm \frac{1}{2}|$ |
| $\psi_3$    | $|\pm 0.035\pm 0.052\pm 0.704\pm \frac{1}{2}|$ |
| $\psi_2$    | $|\pm 0.043\pm 0.079\pm 0.701\pm \frac{1}{2}|$ |
| $\psi_1$    | $|\pm 0.278\pm 0.643\pm 0.091\pm \frac{1}{2}|$ |
| $\psi_0$    | $|\pm 0.290\pm 0.639\pm 0.062\pm \frac{1}{2}|$ |

$\psi$ can be extracted from the crystal field analysis corresponding to the eigenvalue $E_i$. $J^\alpha$ are angular momentum operators associated with the three cartesian coordinates and $n_i, n_j$ are the thermal population factors. The theoretical powder averaged susceptibility is calculated as $\chi = (2\chi(x) + \chi(z))/3$. The inverse susceptibility can then be fitted to $1/\chi$ where $\chi$ is a temperature independent diamagnetic term. The corresponding fitting is shown as the red curve with CEF parameters listed in the caption of Fig. S8 without any additional parameters adjustable parameters except for $\chi_0 = -3.3e-3$ emu/Oe/mol. This consistency with susceptibility data further reinforces our conclusion that $|\pm \frac{1}{2}|$ is the Kramers doublet ground state.

We can extract the inelastic spectral weight for each CEF mode $E_n$ at low temperature $T = 7$ K as following:

$$\delta m_n^2 = 6\mu_B^2\int Q^2\tilde{I}_n(E)(1+e^{-E/k_BT})/r_0F(Q)^2dQdE$$  \text{(S7)}

$\tilde{I}_n(E)$ is momentum-integrated scattering defined in the main text. The sum of the observed inelastic spectral weight $\delta m^2 = 0.37^{2} \mu_B^2$ spin correlation yields a total spectral weight of $m_{\text{tot}}^2 = 6.0(4)$ $\mu_B^2$ per Ce, consistent with the expected value $g_J^2J(J+1) = 6.47\mu_B^2$ with $g_J = \frac{6}{J}$. The magnitude of $\langle \mu_z \rangle$ = $|\langle \psi_0 | g_z | \psi_0 \rangle|$ with the ground state singlet listed in Table S4 is calculated as 0.9 $\mu_B$, while the magnitude of $\langle \mu_z \rangle$ = $|\langle \psi_0 | g_z | \psi_0 \rangle|$ is 0. This is consistent with the proposed in-plane spin structure.

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