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Magnetization and Hall effect studies on the pyrochlore iridate $Nd_2Ir_2O_7$

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We present magnetization and Hall effect measurements on the pyrochlore iridate $Nd_2Ir_2O_7$. Previous muon spin rotation measurements have shown that the system undergoes an unusual transition at $T_M \approx 110$ K into a magnetic phase lacking long-range order, followed by a transition at $T_{\text{LRO}} \approx 6$ K into a state with long-range magnetic order. We observe a small remnant magnetization when cycling through a zero magnetic field at temperatures below T_M. Below T_{LRO}, this remnant magnetization increases sharply, and additional hysteresis effects appear at a higher field $B_c = 2.5$ T, while the Hall resistance develops a nonmonotonic and hysteretic magnetic field dependence, with a maximum at B_c and signatures of an anomalous Hall effect. The dependence on field sweep direction demonstrates a nontrivial transition into a magnetically ordered state with properties paralleling those of known spin-ice systems and suggests a spin reorientation transition across the metal-insulator transition in the *A*-227 series.

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The pyrochlore iridate $A_2Ir_2O_7$ (*A*-227, A = Y, or lanthanide) is an especially appealing system as it allows for the study of the interplay of spin-orbit coupling (SOC), electronic correlations, and band topology. This family has been predicted to host exotic phases including axion insulators, strong topological insulators, and a Weyl semimetal.[1–3] However, aside from the more exotic topological phases predicted in the electronic phase diagram, magnetic frustration also plays a role in the ground state of this system, where both the Ir^{4+} and A^{3+} ions may be magnetic, with each occupying interpenetrating networks of corner-sharing tetrahedra. This potential for magnetic frustration and a corresponding quantum spin-liquid ground state has driven a parallel search for signatures of spin order reflecting the well-studied manifold of spin states on geometrically frustrated tetrahedra intrinsic to spin-ice compounds. Realizing such a state in the presence of strong spin-orbit coupling presents the potential for a host of novel electronic phenomena such as the manifestation of anomalous quantum Hall effects induced via the presence of finite chirality in a spin-liquid state.

Such a state has recently been proposed within the metallic pyrochlore iridate $Pr_2Ir_2O_7$, where a chiral spin-liquid phase is proposed to drive an anomalous Hall response in the absence of conventional, long-range, spin order.[4] How such a response evolves as the bandwidth of this material is tuned and screening or electron hopping effects are reduced, however, remains unexplored. Specifically, one key question remains: whether the proposed chiral spin-liquid phase of Pr-227 evolves continuously into the Mott insulating ground state of the smaller bandwidth *A*-227 systems (e.g., $Y_2Ir_2O_7$, $Eu_2Ir_2O_7$, $Yb_2Ir_2O_7$),[5,6] or whether magnetic interactions are renormalized dramatically near the phase boundary to the insulating regime.

In order to perturb the proposed chiral spin-liquid ground state of Pr-227 via enhanced correlations, one of the most promising avenues is therefore exploring the weakly metallic variants of the $Nd_2Ir_2O_7$ compound, where naively this system is in very close proximity to the spin-liquid ground state of Pr-227. Previously it has been shown that the low energy magnetic and electronic states are related to the *A*-site radii, which set the scale for electron-electron correlations via tuning their resulting bandwidth.[7–9] Specifically, *A*-227 iridates composed of the smallest *A*-site radii (A = Y, Yb-Eu) are insulating for all temperatures, whereas the compound with the largest *A*-site radius, Pr-227, remains metallic down to 30 mK. This leaves Nd-227 as a transitional compound within the *A*-227 series where the resulting ground state (e.g., insulating[10] or weakly metallic[11]) is highly sensitive to the sample stoichiometry.

Our recent measurements on high quality polycrystalline samples of Nd-227 (Ref. 11) revealed weakly metallic behavior which crossed over below 6 K to a logarithmically increasing resistivity with decreasing temperature, as expected for Kondo systems, an effect also observed in Pr-227.[12] The observation of a negative longitudinal magnetoresistance that varies quadratically with magnetization further strengthens the argument for a Kondo-like mechanism.[11] A combination of magnetic susceptibility and zero-field muon spin relaxation studies of this same weakly metallic Nd-227 system revealed short-range or fluctuating order below 110 K with long-range order (LRO) unambiguously observed only below ∼6 K. This demonstrates that the magnetic interactions are appreciably strengthened by the shift in the *A*-site ion from Pr^{3+} to Nd^{3+}, where for Pr-227 the Pr sublattice enters the proposed chiral spin-liquid state[4] below the Curie-Weiss temperature $\theta_{\text{CW}} \sim 1.7$ K; based on the anisotropic response of the magnetization the local spin structure is inferred to be two-in/two-out (2I2O). The resulting complex, weakly metallic, ground state in Nd-227, which preserves a sizable moment on the *R* site and the accompanying f-d exchange interactions, is therefore an ideal setting for probing how increased correlation effects influence the reported chiral spin-liquid phase of Pr-227. Specifically, exploring how the all-in/all-out (AIAO) type spin order proposed for insulating Nd-227 variants[13] compares to our weakly metallic Nd-227 samples may hold important clues for understanding the interactions responsible for the exotic electronic behavior observed in the far metallic Pr-227 region of the *A*-227 phase diagram.

In this Rapid Communication we present detailed measurements of the field dependent hysteresis of bulk magnetization and the Hall effect in poorly metallic Nd-227, whose local field behavior is already known via previously reported muon spin rotation (μSR) measurements. We find a nonzero remnant magnetization on the order of $0.01\mu_B$/Ir below $T_M = 110$ K, a temperature coinciding with the bifurcation in magnetic susceptibility observed in our prior work. Below $T \sim 10$ K, a second hysteresis centered about a critical field $B_c \sim 2.5$ T is also observed, coinciding with a sharp increase in the zero-field remnant magnetization. In addition to the large negative magnetoresistance below 10 K, we find a striking nonmonotonic Hall effect that shows considerable hysteresis peaked at B_c. Our results provide evidence that the spin behavior and electronic response of Nd-227 manifests as a precursor phase intermediate between the long-range ordered Eu-227 and the disordered chiral spin liquid of Pr-227. Furthermore, our data suggest that the "all-in/all-out" spin configuration previously reported in more insulating Nd-227 variants reorients into a "two-in/two-out" spin-ice configuration across the metal-insulator transition (MIT) within the A-227 series.

Polycrystalline samples of $Nd_2Ir_2O_7$ were synthesized by reacting stoichiometric amounts of Nd_2O_3 (99.99%) and IrO_2 (99.9%) as previously described.[11] Magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System (MPMS) superconducting quantum interference device (SQUID) magnetometer. Data for isothermal hysteresis loops were taken by cooling the sample in a nominal zero field, and sweeping the field over the cycle $0 \rightarrow 5 \rightarrow -5 \rightarrow 0.1$ or 5 T. Individual data points were taken while sweeping the magnetic field at a constant rate of 70 mT/min. The sample was warmed to $T = 130\ \mathrm{K} > T_M$ after each isothermal run. Magnetotransport was measured at and above 2 K in a Quantum Design Physical Property Measurement System (PPMS), and below 2 K in a ^{3}He cryostat with a 9 T magnet. Several pressed samples prepared from independent batches were studied; all were polished into bar geometries with typical sample thicknesses in the range 0.5–1 mm. For Hall effect measurements, two contacts were placed at sample edges perpendicular to both the current flow and field directions, while for longitudinal magnetoresistance measurements the Hall voltage was shorted with the voltage leads extending across the sample, and the magnetic field was applied parallel to the current direction.

In Fig. 1 we show the magnetization at $T = 2$ K over the field cycle $0 \rightarrow 5 \rightarrow -5 \rightarrow 0.1$ T. Data are presented as μ_B per Ir, although our earlier work[11] showed that paramagnetic Nd^{3+} makes a large contribution to the total magnetization. A small hysteresis loop centered on zero field (lower right inset) is seen with a zero-field moment of $\pm 0.015\mu_B$/Ir, roughly three orders of magnitude larger than that observed for Y-227 in the long-range ordered state near 100 K as reported in Ref. 14, and two orders of magnitude larger than measured by us on our own Y-227 samples.[15] Also evident is a hysteresis loop centered on a field value $-B_c \approx -2.5$ T. The magnitude of the hysteresis is 2.5 times larger than that at zero field. Measurements over the field cycle $0 \rightarrow 5 \rightarrow -5 \rightarrow 5$ T at $T = 3$, 4, and 5 K show that the hysteresis occurs at both positive and negative values of B_c. Plotting the derivative

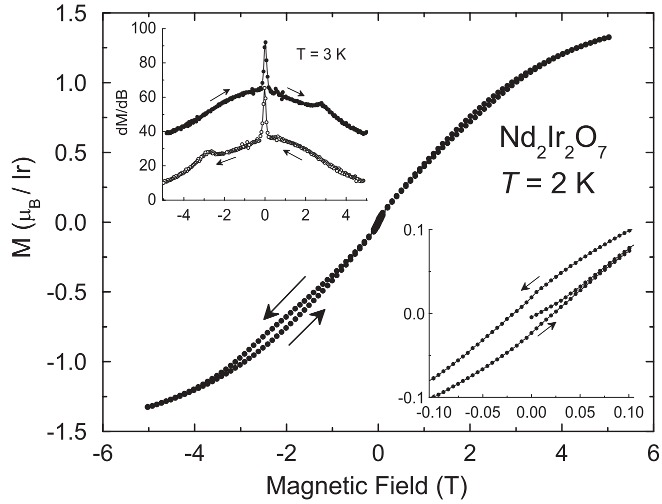

FIG. 1. Magnetization hysteresis loop for $Nd_2Ir_2O_7$, with a field cycle of $0 \rightarrow 5 \rightarrow -5 \rightarrow 0.1$ T. Lower right inset: Closeup of the hysteresis in the vicinity of zero field. Upper left inset: Derivative dM/dH (in units of $10^{-2}\mu_B/T$) for $5 \rightarrow -5$ T (lower curve) and -5 to 5 T (upper curve), taken at $T = 3$ K.

dM/dB for the up and down field sweeps (upper left inset) shows that a peak occurs at a field of magnitude B_c and pointing opposite to the previous magnetizing field direction, that is, at $+B_c$ for the field sweep -6 to 6 T, and at $-B_c$ for 6 to -6 T. The virgin curve $0 \rightarrow 6$ T also shows a peak in dM/dB at B_c (not shown), but with a size about one-half those depicted in the inset. This behavior is not typical for metamagnetic transitions (e.g., spin flip or spin flop), which typically occur at $\pm B_c$ for both sweep directions, with potentially some small hysteresis about that value.

In Fig. 2 we have plotted the temperature dependence of the difference between the down and up sweep magnetizations, $\Delta M = M_{\mathrm{down}}(B) - M_{\mathrm{up}}(B)$ for zero field [ΔM_{ZF} in Fig. 2(a)] and at B_c [ΔM_{HF} in Fig. 2(b)]; the insets show representative curves taken at several temperatures. In Fig. 2(a) we see two abrupt changes in ΔM_{ZF}, near 110 and 10 K. These correspond closely to the two transitions observed in our earlier μSR, transport, and dc susceptibility results,[12] $T_M \approx 110$ K and $T_{\mathrm{LRO}} \approx 6$ K, corresponding to the onset of short-and long-range magnetic order, respectively. We also note that two transitions were observed in Y-227, with $T_M \approx 190$ K and $T_{\mathrm{LRO}} \approx 150$ K,[5] and the results for the temperature dependence of the remnant moment reported in Ref. 15 on that system are similar to our results shown in Fig. 2(a) and consistent with those transition temperatures.

From Fig. 2(b) we see that as the temperature decreases below 10 K, ΔM_{HF} increases rapidly from zero, and so we assume the onset of hysteresis at B_c is associated with the onset of long-range magnetic order at T_{LRO}. A high field hysteresis was observed in Pr-227 below the spin freezing temperature for fields applied along the [111] direction only,[4] however, as full hysteresis loops have not been published on that system, it is unknown if a similar behavior with regard to the field sweep direction exists in Pr-227 as well. Regardless, it was estimated, based on the size of the localized Pr^{3+} moments, that the hysteresis corresponded to a partial stabilization of three-in/one-out (3I1O) within the

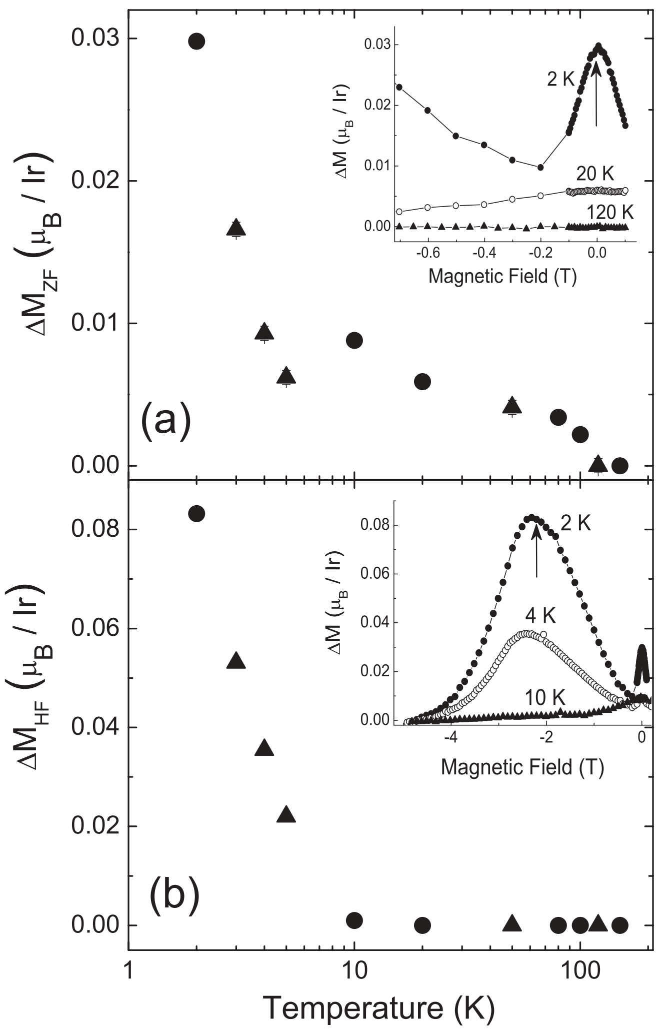

FIG. 2. (a) Temperature variation of the maximum in $\Delta M = M_{\mathrm{down}} - M_{\mathrm{up}}$ at zero field. The inset shows detailed curves for ΔM in the vicinity of zero field at three temperatures. (b) Temperature variation of the maximum in ΔM near -2 T. The inset shows typical curves for ΔM at three temperatures. Different symbols (solid circles, solid triangles) represent data taken on different experimental runs.

two-in/two-out (2I2O) matrix below the spin freezing temperature, consistent with Monte Carlo simulations incorporating Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions on the pyrochlore lattice.[16] Measurements of the magnetization of the insulating spin-ice compound $Ho_2Ti_2O_7$ at low temperatures have also shown transitions from 2I2O to 3I1O at high fields applied along the [111] direction, which are hysteretic in nature.[17] We have also made a preliminary measurement of the magnetocaloric effect on Nd-227 at $T = 0.5$ K,[15] and find a large heat release at B_c, which has the same field history dependence as shown in the upper inset of Fig. 1. We conclude that the magnetization hysteresis at B_c is the signature of entry into a lower entropy magnetically ordered state, e.g., a 2I2O to 3I1O or AIAO transition.

We now describe our Hall effect results. Due to imperfect alignment and probable current flow irregularities in the sintered samples, our signal had a large contribution from the resistance [Fig. 3(a)]. The Hall voltage was extracted by taking the antisymmetric part of the measured voltage and then examining the field history dependence. This was done for field sweeping from -6 to 6 T and also from 6 to -6 T. At 10 K the magnetic field response is dominated by the Hall contribution because the resistance is essentially field independent, but at lower temperatures the magnetoresistance is large,[11] and so the Hall (antisymmetric) component is only 4% of the total change. Because the Hall signal is a relatively small fraction of the total signal, we independently measured the longitudinal magnetoresistance;[15] no asymmetry is observed with respect to the field, and any hysteresis observed between the sweep directions near B_c was near the limits of the experimental error. We note that the offset at zero field between the virgin zero field cooled and zero field after ramping to 6 T was observed in both Hall and longitudinal geometries.

The field dependence of the Hall resistivity is shown in Fig. 3(b) with each isotherm offset for clarity. While at temperatures higher than 10 K the signal is linear and nearly independent of field sweep direction, at lower temperatures we find a nonmonotonic variation of the Hall resistivity with field, with strong field history dependence. In Figs. 3(c) and 3(d) we show the reversible and irreversible components of the field dependence of ρ_{xy}; these are found by taking half of the sum (reversible) or difference (irreversible) of the forward and backward sweep directions shown in Fig. 3(b) for each temperature. The magnetic field dependence of the reversible component is characteristic of an anomalous Hall effect (AHE), which is expected in a system with magnetic ordering and strong spin-orbit coupling, as discussed below. In this case, we can find the approximate carrier concentration by fitting the reversible part of the data at high fields ($B > 4$ T) where M has nearly saturated, allowing us extract a lower limit on R_0. Using the single band approximation, $R_0 = -1/ne$, and we find an upper limit of the carrier concentration of 2.5×10^{20} cm^{-3}, compared to 4×10^{21} cm^{-3} measured in small single crystals of Pr-227.[18] This confirms our expectation that Nd-227 exhibits properties that are intermediate between those of metallic Pr-227 and the insulating members of the A-227 family. Following the arguments of Ref. 18, and assuming a spherical Fermi surface with $k_F = (3\pi^2 n)^{1/3}$, we find the resultant RKKY interaction between neighboring Nd^{3+} ions to be ferromagnetic, as in the case of Pr-227.

These results are remarkably similar to those obtained in artificial spin-ice structures[19] for which the field dependence of the reversible component of the Hall resistance is that typically associated with an AHE in ferromagnetic metals,[20] and the irreversible component develops a peak about a critical field B_c with decreasing temperature. Magnetization extracted from magnetotransport in Ref. 19 shows a sharp change in dM/dH about the critical field, which also depends on the field sweep direction in a manner similar to what we have observed in Nd-227. These features were attributed to a spatially varying chirality around each hexagonal loop in the kagome lattice studied in that work, and therefore may be directly related to phenomena observed in the conducting pyrochlore compounds which have a spin-ice configuration.

The similarities between the field dependence of the magnetization and the Hall effect shown here for Nd-227 and those of other spin-ice compounds strongly imply that the magnetic ground state of Nd-227 in the weak metallic phase is of the 2I2O spin-ice type rather than AIAO, as

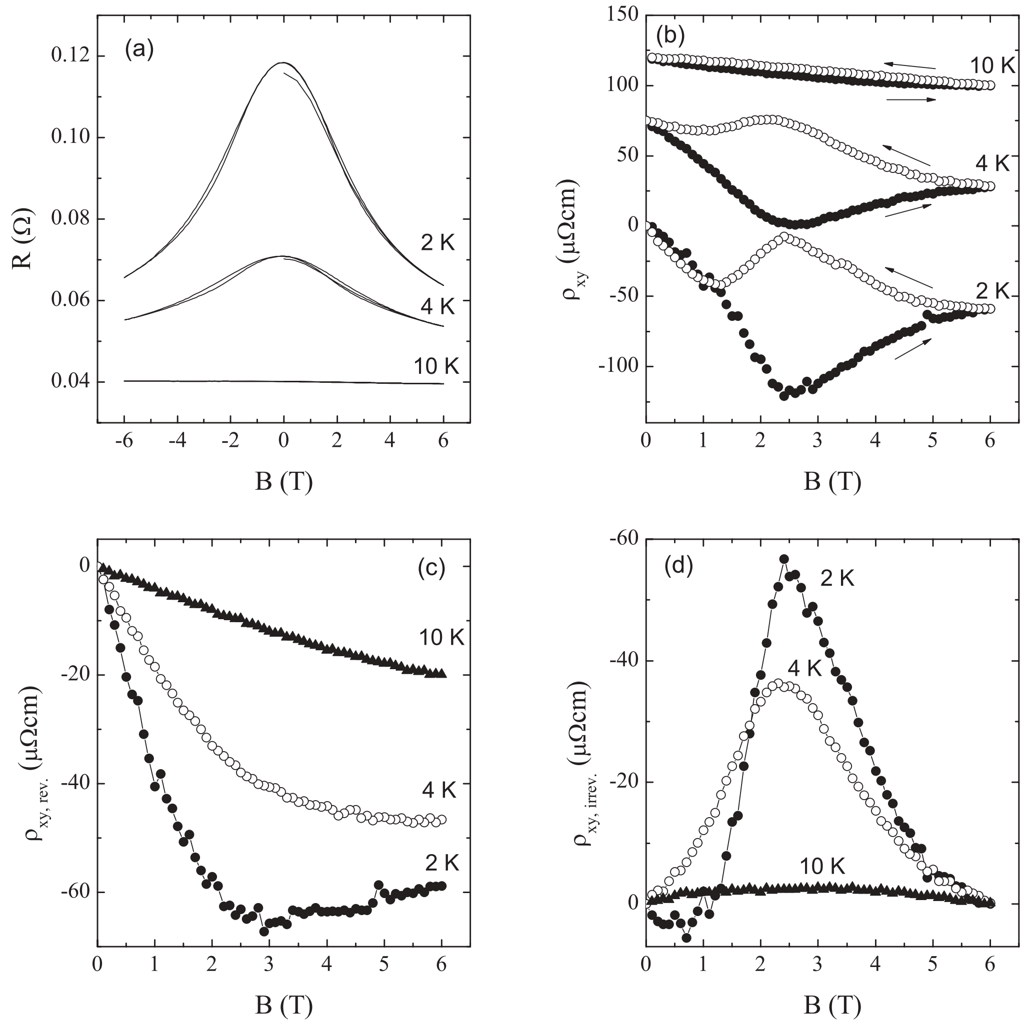

FIG. 3. (a) Resistance vs magnetic field for a sample in the transverse geometry over the cycle $6 \rightarrow -6 \rightarrow +6$ T at several temperatures. (b) Hall resistivity extracted from the antisymmetric part of the curves in (a) from $6 \rightarrow -6$ T (open symbols, left-pointing arrows) and $-6 \rightarrow 6$ T (solid symbols, right-pointing arrows). The curves at 4 and 10 K are offset by 0.11 and 0.22 $\mu\Omega$ cm, respectively, for clarity. The (c) reversible and (d) irreversible components of the Hall resistivity extracted from the curves in (b), as described in the text.

previously considered for more insulating Nd-227 variants. Recent theoretical work incorporating f-d exchange supports a 2I2O ground state for a wide range of coupling parameters, particularly if the average (Curie-Weiss) interaction between the neighboring Nd^{3+} is ferromagnetic.[21] The spin-ice state in the iridates has theoretically been shown to exhibit a transition into a number of more ordered phases at high magnetic fields including the kagome-ice state,[22] 3I1O, and even AIAO,[23] depending on the conduction electron density and strength of distant-neighbor interactions. It has also recently been predicted that spin-ice structures may give rise to a resistivity minimum as in traditional Kondo systems,[24] and in fact it was shown[25] to agree with previous data for single crystal samples made metallic though applied external pressure.[26] To our knowledge it has not been demonstrated either theoretically or experimentally that any of these phenomena will occur if the system is in an AIAO ground state.

Despite these similarities, the presence of LRO in zero field as observed in μSR measurements is inconsistent with that of traditional spin-ice behavior and the chiral spin-liquid state proposed within Pr-227. One possible explanation for this behavior is that the onset of hysteresis at zero field below T_M and near B_c below $T_{\rm LRO}$ corresponds to distinct order parameters, such as order of the individual sublattices mediated by d-d, f-f, or f-d interactions. We note that these two temperatures are similar to that found in the Yb-227, in which the Ir^{4+} moments order at $T_{\rm LRO} = 125$ K, while the localized paramagnetic Yb^{3+} moments become polarized due to this local field and interact with an effective Curie-Weiss temperature of $\theta_{\rm CW} \sim -7$ K,[5] with probable ordering in the Yb sublattice below 3 K.[15] Therefore with the addition of the RKKY interaction in Nd-227, we expect there should be significantly more impact beyond simple polarization on the underlying ground state of the Ir sublattice and vice versa. It is also possible that at low temperatures and zero magnetic field the ordering is incomplete, producing an electronically phase-separated heterogeneous state composed of domains long-range magnetic order imbedded within a matrix of short-range ordered material, as proposed for the Pr-227.[4] Indeed, our μSR measurements[11] show that the depolarization in zero field does not follow the form typically associated with simple LRO, as seen in the insulating A-227 compounds,[5,6] requiring an additional component which could be associated with the domains of short-range order.

In summary, we have studied high quality polycrystalline Nd-227 via magnetization and the Hall effect. Our combined results reveal a complex precursor phase in the A-227 series at the boundary between the proposed metallic spin liquid and the long-range antiferromagnetic ordered insulating phase where signatures of time reversal symmetry breaking emerge prior to the onset of static spin order. This intermediate state manifests electronic behavior reflecting the presence of two field and temperatures scales, suggesting two order parameters in this system. The striking similarities of our results with those for other spin-ice systems suggests that Nd-227 in the weakly metallic regime has a two-in/two out rather than all-in/all-out magnetic structure, potentially implying a spin reorientation transition across the MIT in the A-227 series.

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