Abstract: The nickelate Pr4Ni3O8 features quasi-two-dimensional layers consisting of three stacked square-planar NiO2 planes, in a similar way to the well-known cuprate superconductors. The mixed-valent nature of Ni and its metallic properties makes it a candidate for potentially unconventional superconductivity. We have synthesized Pr4Ni3O8 by topotactic reduction of Pr4Ni3O10 in 10% hydrogen gas, and report on measurements of powder-neutron diffraction, magnetization, and muon-spin rotation (µSR). We find that Pr4Ni3O8 shows complicated spin-glass behavior with a distinct magnetic memory effect in the temperature range from 2 to 300 K and a freezing temperature Ts=68K. Moreover, the analysis of µSR spectra indicates two magnetic processes characterized by remarkably different relaxation rates: a slowly relaxing signal, resulting from paramagnetic fluctuations of Pr/Ni ions, and a fast-relaxing signal, whose relaxation rate increases substantially below 70K which can be ascribed to the presence of short-range correlated regions. We conclude that the complex spin-freezing process in Pr4Ni3O8 is governed by these multiple magnetic interactions. It is possible that the complex magnetism in Pr4Ni3O8 is detrimental to the occurrence of superconductivity.

DOI: https://doi.org/10.1103/physrevb.102.054423

Originally published at:
Huangfu, Shangxiong; Guguchia, Zurab; Cheptiakov, Denis; Zhang, Xiaofu; Luetkens, Hubertus; Gawryluk, Dariusz Jakub; Shang, Tian; von Rohr, Fabian O; Schilling, Andreas (2020). Short-range magnetic interactions and spin-glass behavior in the quasi-two-dimensional nickelate Pr4Ni3O8. Physical review B, 102(5):054423. DOI: https://doi.org/10.1103/physrevb.102.054423
Short-range magnetic interactions and spin-glass behavior in the quasi-two-dimensional nickelate Pr$_4$Ni$_3$O$_8$

Shangxiong Huangfu, Zurab Guguchia, Denis Cheptiakov, Xiaofu Zhang, Hubertus Luetkens, Dariusz Jakub Gawryluk, Tian Shang, Fabian O. von Rohr, and Andreas Schilling

1Department of Physics, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland
2Laboratory for Muon Spin Spectroscopy (LMU), Paul Scherrer Institute (PSI), Forschungsstrasse 111, CH-5232 Villigen, Switzerland
3Laboratory for Neutron Scattering and Imaging (LINS), Paul Scherrer Institute (PSI), Forschungsstrasse 111, CH-5232 Villigen, Switzerland
4Laboratory for Multiscale Materials Experiments (LMX), Paul Scherrer Institute (PSI), Forschungsstrasse 111, CH-5232 Villigen, Switzerland
5Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

(Received 26 May 2020; revised 16 July 2020; accepted 20 July 2020; published 17 August 2020)

DOI: 10.1103/PhysRevB.102.054423

The nickelate Pr$_4$Ni$_3$O$_8$ features quasi-two-dimensional layers consisting of three stacked square-planar NiO$_2$ planes, in a similar way to the well-known cuprate superconductors. The mixed-valent nature of Ni and its metallic properties makes it a candidate for potentially unconventional superconductivity. We have synthesized Pr$_4$Ni$_3$O$_8$ by topotactic reduction of Pr$_2$Ni$_3$O$_6$ in 10% hydrogen gas, and report on measurements of powder-neutron diffraction, magnetization, and muon-spin rotation ($\mu$SR). We find that Pr$_4$Ni$_3$O$_8$ shows complicated spin-glass behavior with a distinct magnetic memory effect in the temperature range from 2 to 300 K and a freezing temperature $T_f \approx 68$ K. Moreover, the analysis of $\mu$SR spectra indicates two magnetic processes characterized by remarkably different relaxation rates: a slowly relaxing signal, resulting from paramagnetic fluctuations of Pr/Ni ions, and a fast-relaxing signal, whose relaxation rate increases substantially below $\approx 70$ K which can be ascribed to the presence of short-range correlated regions. We conclude that the complex spin-freezing process in Pr$_4$Ni$_3$O$_8$ is governed by these multiple magnetic interactions. It is possible that the complex magnetism in Pr$_4$Ni$_3$O$_8$ is detrimental to the occurrence of superconductivity.

Copper-based high-temperature superconductors show quasi-two-dimensional (2D) structural and electrical properties. They contain CuO$_2$ planes with Cu in a mixed-valent $3d^{9-8}$ configuration, and exhibit considerable antiferromagnetic correlations [1,2]. Even before [3] but also soon after their discovery [4], structurally similar layered nickelates have been proposed to be potential superconductors [5]. The rare-earth (Ln) nickelates Ln$_{n+1}$NiO$_{2n+2}$ exhibit such a 2D layered structure. They contain $n$ stacked square-planar NiO$_2$ planes, alternating with Ln/O$_2$/Ln fluoride-type layers, which is reminiscent to the configuration of the CuO$_2$ planes in electron-doped cuprate superconductors [6–8]. The mixed-valence state of Ni ion between $3d^8$ and $3d^9$ in these nickelates, with a formal Ni valence of $1+1/n$, resembles the situation in heavily hole-doped cuprates [9–12]. Therefore, these nickel oxides have been considered as promising candidates for new superconductors [13]. Indeed, superconductivity has very recently been found in thin films of the “infinite layer” compound Nd$_{1-y}$Sr$_y$NiO$_2$ ($n=\infty$) [14–16]. To synthesize these structures, one of the common synthesis techniques is to first prepare $T$-type materials containing NiO$_6$ octahedra, and to subsequently reduce them via a low-temperature topotactic reaction to obtain $T'$-type structures with square-planar NiO$_2$ planes [7,17,18].

The related nickelate LaNiO$_2$ [7,17] is paramagnetic with apparently two different magnetic regimes (above and below $T \approx 150$ K, respectively), with no signs of magnetic order [7]. Likewise, the isostructural NdNiO$_2$ does not show any signs of long-range magnetic order down to $T \approx 1.7$ K [19]. La$_3$Ni$_2$O$_6$ is the only known member of the Ln$_{n+1}$NiO$_{2n+2}$ series with a bilayer ($n=2$) structure [10]. Nuclear magnetic resonance (NMR) measurements down to 5 K showed the presence of antiferromagnetic spin fluctuations [20], although no long-range magnetic order develops. The trilayer ($n=3$) versions, Ln$_3$Ni$_3$O$_8$ ($Ln=La$, Pr, and Nd/Sm) to be discussed here, have an average Ni valence of +4.3. La$_3$Ni$_3$O$_8$ shows a sharp phase transition from a high-temperature paramagnetic semiconducting phase to a low-temperature antiferromagneticlike insulating phase around $T \approx 105$ K [11], which has also been studied by muon-spin rotation ($\mu$SR) techniques [21]. NMR measurements revealed 2D antiferromagnetic fluctuations [22], and both magnetic and charge-ordering phenomena were inferred from x-ray and neutron-diffraction (ND) measurements [23,24]. Semiconductive behavior has also been reported for Nd$_{3.5}$Sm$_{0.5}$Ni$_3$O$_8$, with a trend to increasing metallicity under pressure [25], while the metallicity of Pr$_4$Nd$_{4-z}$Ni$_3$O$_8$ was reported to increase with Pr content $z$ [26].

By very contrast, Pr$_4$Ni$_3$O$_8$ is metallic (but not superconducting) at ambient pressure between 2 and 300 K, without any signs for a possible phase transition, neither from transport nor from heat-capacity measurements [12]. At present, very little is known about the magnetic behavior of this compound. We have, therefore, performed a series of powder
ND, magnetization, and μSR measurements on Pr$_3$Ni$_3$O$_8$ powders.

We first synthesized high-quality powdered samples of Pr$_3$Ni$_3$O$_8$ according to the method described in Refs. [27] and [28]. Subsequent thermogravimetric experiments suggest a resulting oxygen content of 7.98(4). The high quality of the thus obtained Pr$_3$Ni$_3$O$_8$ powder was confirmed by x-ray diffraction (XRD) and powder-ND measurements (Figs. S1–S3 in the Supplemental Material [29]) [30–32] without any indication for impurities within the detection limit. The ND measurements were performed at $T = 1.5$ and 300 K and the zero-field (ZF) μSR experiments between 5 and 300 K. The quasistatic (DC) and the alternating current (AC) magnetization were studied from 2 to 350 K and from 2 to 300 K, respectively. To cross-check the magnetic data, some of the Pr$_3$Ni$_3$O$_8$ powder was reversibly transformed back into Pr$_3$Ni$_3$O$_{10}$. Details about sample preparation and the subsequent characterization are given in the Supplemental Material [29].

ND techniques not only probe purity and quality of crystalline compounds, but can also reveal their magnetic structure. Apart from a shift of the nuclear peaks with temperature, our corresponding refinements [29] do not indicate any long-range ferromagnetic or antiferromagnetic orders in the temperature range between 1.5 and 300 K.

To study the magnetic properties further, we performed DC magnetization measurements by collecting temperature-dependent field-cooling (FC) and zero-field cooling (ZFC) magnetization $M(T)$ data in various external magnetic fields, see Figs. 1(a) and S6 [29], and by measuring magnetization $M(H)$ loops at different temperatures [Fig. 1(b)]. The magnetization $M$ of Pr$_3$Ni$_3$O$_8$ shows a similarly complex behavior as other $T^*$-type nickelates [21–23]. While in magnetic fields larger than $\mu_0H \approx 0.5$ T, $M(T)$ appears to be reversible within the resolution of the measurement, FC and ZFC data gradually separate with decreasing $H$. In $\mu_0H \approx 0.01$ T, the corresponding $M(T)$ curves are separated up to the highest investigated temperature $T = 350$ K. In $\mu_0H > 1$ T, a broad, peaklike structure develops that becomes more pronounced with increasing field, in a similar fashion as has been observed in La$_3$Ni$_2$O$_6$ and attributed to the presence of superparamagnetic Ni particles [10], although the feature is much broader in our Pr$_3$Ni$_3$O$_8$ data than in La$_3$Ni$_2$O$_6$. The corresponding maximum in $M(T)$ shifts from $T \approx 67$ K for $\mu_0H = 1$ T to $\approx 85$ K in 7 T. In Fig. 1(b), we show corresponding magnetization $M(H)$ loops taken at different temperatures. The data are hysteretic at all $T$, with coercivities ranging from $\approx 0.044$ T at 2 K to $\approx 0.011$ T at room temperature, and a remanent magnetization of the order of $\approx 1200$ emu mol$^{-1}$ at 2 K and $\approx 550$ emu mol$^{-1}$ at room temperature [lower inset of Fig. 1(b)], respectively, which is reminiscent of ferromagnetic-like behavior.

We can interpret these data as a superposition of a ferromagnetic-like contribution that is saturating in high enough fields, and a paramagnetic term that is linear in $H$ as has been done, e.g., for NdNiO$_2$$_{1+y}$ [19]. In Fig. 2 we show the temperature dependence of both contributions. The high-temperature part of the linear paramagnetic susceptibility above $\approx 160$ K can be well fitted by a Néel-type law, $\chi_{\text{para}}(T) = C/(T + \Theta) + \chi_0$, with a Curie constant $C \approx 6.8$ emu K Oe$^{-1}$ mol$^{-1}$, a Pauli-paramagnetic susceptibility $\chi_0 \approx 10^{-3}$ emu Oe$^{-1}$ mol$^{-1}$, and $\Theta \approx 160$ K. If we assume the free-ion value for the magnetic moment of Pr$^{3+}$ (3.58 $\mu_B$) as has been found in Pr$_3$Ni$_3$O$_{10}$ [26,27], we obtain a residual magnetic moment of $\approx 1.70 \mu_B$. This value would be consistent with the localized moment of one spin-1/2 Ni$^+$ ion, but most probably rather represents an average over the three Ni sites [12], with some delocalized 3d electrons that lead to the observed metallic behavior. In the high-temperature range above $\approx 150$ K, the saturated magnetic moment $M_{\text{sat}}$ (inset of Fig. 2) can be well fitted by a $1 - (T/T^*)^{1/2}$ law, with an extrapolated zero-temperature magnetic moment of $\approx 0.22 \mu_B$ mol$^{-1}$ and $T^* \approx 1100$ K.

FIG. 1. (a) Temperature-dependent ZFC and FC magnetization $M(T)$ measurements on Pr$_3$Ni$_3$O$_8$ in various external magnetic fields up to $\mu_0H = 7$ T; arrows indicate the direction of the measurements; some data have been multiplied by a factor for clarity. (b) Isotherm magnetization $M(H)$ loops with magnetic fields ranging from $\approx 7$ to 7 T at temperatures between 2 and 350 K; the lower inset is in an expanded scale to show the hysteretic behavior in low magnetic fields, while the upper inset shows corresponding data for 10 and 350 K for Pr$_3$Ni$_3$O$_8$ (dashed lines) in comparison with back-oxygenated Pr$_3$Ni$_3$O$_{10}$ from Pr$_3$Ni$_3$O$_{10}$ (open symbols with no detectable hysteresis) and the original Pr$_3$Ni$_3$O$_{10}$ powder (solid lines); arrows indicate the direction of the measurements.
If this large saturated magnetic moment were due to impurities (e.g., Ni particles as suggested in Ref. [10], with \(M_{\text{sat}} = 0.66 \mu_B \text{mol}^{-1}\), \(\approx 10\% \) of Pr\(_3\)Ni\(_8\)O\(_{10}\) must have been decomposed during the topotactic reduction to Pr\(_3\)Ni\(_8\)O\(_{10}\) since the original Pr\(_3\)Ni\(_8\)O\(_{10}\) powder showed neither magnetic hysteresis nor saturation. Such a significant decomposition should have manifested itself in our x-ray and ND data, however, which is not the case. To further cross-check our \(M(H)\) data, we transformed Pr\(_3\)Ni\(_8\)O\(_{10}\) back into pure-phase Pr\(_3\)Ni\(_8\)O\(_{10}\), see upper inset of Fig. 1(b) and Supplemental Material [29]. The resulting magnetization \(M(H)\) curves are identical to those of the original Pr\(_3\)Ni\(_8\)O\(_{10}\) powder. The ferromagnet-like hysteretic behavior completely vanished, and it must therefore be intrinsic to Pr\(_3\)Ni\(_8\)O\(_{10}\).

As the DC magnetization data are clearly hysteretic, we performed additional time-dependent magnetization experiments, namely AC magnetic susceptibility measurements in zero static external magnetic field, and aging and memory experiments for the DC magnetization. We observe a broad peak in the temperature-dependent real part of the AC susceptibility \(\chi'(T)\) for all AC frequencies \(f\) between 2 and 300 Hz, as shown in Figs. 3(a) and S7 [29]. Moreover, the peak positions shift from \(\approx 74\) to \(\approx 89\) K with increasing \(f\), while the peak amplitudes decrease gradually, indicating a possible spin-glass freezing below the respective peak temperatures. Aging and memory measurements taken in a FC protocol also show a clear time and history dependence of the DC magnetization (see the Supplemental Material [29]), which is regarded as an experimental signature for spin-glass behavior [33]. Figure 3(b) shows the intermittent-stop cooling (ISC) data taken in \(\mu_B H = 5\) mT. In these measurements, \(H\) was switched from this value to zero, followed by a waiting period of 5000 s at constant temperature. During this time, the magnetization changed slowly with a time constant of several minutes [upper inset of Fig. 3(b)]. After that process, the magnetic field was switched back to 5 mT and the sample was further cooled down to the next temperature. In spin glasses, the spin dynamics is known to slow down as the freezing temperature \(T_f\) is approached, which impedes the magnetization recovery and leads to large magnetization steps in such ISC curves [34]. Indeed, these steps are largest between 30 and 50 K, and become smaller with increasing temperature but remain finite up to room temperature [lower inset of Fig. 3(b)]. Although \(T_f\) appears to have a finite value around \(\approx 70\) K (see below), the continuous slow freezing process persists down to the lowest investigated temperature (5 K). Upon warming the sample continuously up (continuous warming, CW) in the same constant magnetic field after such an ISC process, \(M(T)\) exhibits pronounced kink-like features at each of the previous intermittent-stopping temperatures, indicating a distinct memory effect that is characteristic for many spin-glasses, including some nickel oxides [33,35,36].

To analyze the frequency dependence of the peaks in \(\chi'(T)\) [inset of Fig. 3(a)], we may use a critical dynamical
suggests that the behavior of Pr$_4$(O$_{39}$)

shows corresponding spectra collected between $2$ and $39$.

z′ (inset of Fig. 3(a)) suggests that the behavior of Pr$_4$Ni$_3$O$_8$ can be well described by this model with $T_\text{f} = 68.3 \pm 0.3$ K, $z\nu = 3.8 \pm 0.2$, and $\tau_0 \approx 10^{-6}$ s. The exponent $z\nu$ is just in the range of normal glassy systems where $z\nu = 4 - 12$ [38]. The flip time $\tau_0$ falls in the order of magnitude $10^{-6} - 10^{-9}$ s determined by the atomic spin-flip time [39]. Another way to analyze the frequency dependence of the peaks in $\chi'(T)$ is to apply the Vogel-Fulcher model, which characterizes a continuous freezing crossover into a low-temperature glassy regime [39,40], $\tau = \tau_0 \exp[E_a/k_B(T - T_0)]$, where $E_a$ is an energy barrier, $k_B$ is the Boltzmann constant, and $T_0$ is a characteristic temperature which is usually below the freezing temperature. The dashed line in the inset of Fig. 3(a) indicates that the same data can be well described by this model as well, with $T_0 = 60.1 \pm 0.8$ K $< T_\text{f}$, $E_a/k_B \approx 130$ K and $\tau_0 \approx 10^{-6}$ s. The energy barrier fulfills $E_a/k_B \approx 2T_\text{s}$, as observed in other spin-glasses [41]. We conclude that Pr$_4$Ni$_3$O$_8$ indeed shows spin-glass behavior with a freezing temperature $T_\text{f} \approx 68$ K, which is consistent with the pronounced aging and memory effects that become most significant below $\approx 80$ K [lower inset of Fig. 3(a)]. Below $T_\text{s}$, the saturated magnetic moment (inset of Fig. 2) also strongly increases with decreasing temperature down to the lowest investigated temperature.

To further characterize the complex magnetic behavior in Pr$_4$Ni$_3$O$_8$, we performed additional ZF-$\mu$SR measurements, where positive muons are implanted into a sample and serve as an extremely sensitive local probe to detect small internal magnetic fields and ordered magnetic volume fractions in the bulk of magnetic materials. Thus, ZF-$\mu$SR is particularly powerful to study inhomogeneous magnetism in materials. Figure 4(a) shows corresponding spectra collected between 5 and 300 K. Different from La$_4$Ni$_3$O$_8$ [21], the ZF-$\mu$SR data in Pr$_4$Ni$_3$O$_8$ do not show any oscillations over the whole measured temperature range. This indicates the absence of long-range magnetic order in Pr$_4$Ni$_3$O$_8$ down to 5 K, in agreement with our ND result. The spectra show an initial fast decay and then a much slower one. The best fit to these spectra is achieved with two exponential paramagnetic responses with different relaxation rates [42-44], $A(t) = A_0 + A_{\text{fast}} \exp(-\lambda_{\text{fast}} t) + A_{\text{slow}} \exp(-\lambda_{\text{slow}} t)$. The last two terms represent the fast and the slow relaxation, respectively, with the relaxation rates $\lambda_{\text{fast}}$ and $\lambda_{\text{slow}}$ for each component, and an additional constant offset $A_0$. In Figs. 4(b) and 4(c), three different regimes can be clearly distinguished: (i) the temperature range 300–150 K, in which the relaxation rate of the fast component $\lambda_{\text{fast}}$ shows a weak temperature dependence; (ii) below $\approx 150$ K, where $\lambda_{\text{fast}}$ starts to increase from $\approx 0.8$ $\mu$s$^{-1}$ at $\approx 150$ K to $\approx 3$ $\mu$s$^{-1}$ at $\approx 70$ K; and (iii) below $\approx 70$ K, where $\lambda_{\text{fast}}$ shows a strong increase and reaches an almost saturated value of $\approx 38$ $\mu$s$^{-1}$ at 5 K. The rate $\lambda_{\text{slow}}$ also shows a weak $T$ dependence down to $\approx 150$ K, below which it increases from $\approx 0.1$ to $\approx 0.86$ $\mu$s$^{-1}$ at 5 K. We note that the lowest value $\lambda_{\text{fast}}$ is still much higher than the corresponding value of $\lambda_{\text{slow}}$. Such a remarkable difference rules out the origin of these two decays being due to slight inhomogeneities, such as a compositional distribution within the polycrystalline sample, temperature gradients, or any other.

FIG. 4. (a) Zero-field $\mu$SR spectra at 5, 50, 100, 150, and 300 K; the relaxation rates of the fast component (b) and of the slow component (c) as functions of temperature are calculated from the corresponding $\mu$SR asymmetry spectra; the inset of (b) is in an expanded scale to show the fast component relaxation rate at high temperatures; arrows mark the change of the relaxation rate.
small spatial variations. While it is plausible to identify $\lambda_{\text{slow}}$ as originating from the paramagnetism in Pr$_3$Ni$_5$O$_8$, i.e., the fluctuations of Pr/Ni ions in the paramagnetic state, the strong quantitative difference between the relaxation rates $\lambda_{\text{fast}}$ and $\lambda_{\text{slow}}$ indicates the presence of another source of fast muon depolarization, which is different from pure paramagnetism. In general, a fast-relaxing decay indicates the presence of strong spin-spin correlations. Stronger magnetic correlations between the spins slow down the spin fluctuations, leading to a significant rise of the relaxation rate. Thus, our $\mu$SR results indicate the slowing down of spin fluctuations starting already below $\approx 150$ K, and the formation of strong short-range-order correlations below $\approx 70$ K. This is consistent with the formation of a spin-glass-like state below this temperature, most likely due to the presence of short-range-ordered magnetic clusters or islands, and we estimate the volume fraction of this state to $\approx 40\%$ at 5 K.

The quantities $\chi_{\text{para}}$, $\lambda_{\text{fast}}$ and $\lambda_{\text{slow}}$ all show changes in their $T$ dependencies already at $\approx 150$ K besides those at $T_c$. This may indicate a further transition (or crossover) taking place around this temperature, the origin of which is unknown to us at present. The change of the Néel-type magnetic susceptibility $\chi_{\text{para}}(T)$ below $T \approx \theta \approx 160$ K is too large to be solely ascribed to the nickel subsystem. It is conceivable that a that large volume fraction in the system Pr$_3$Ni$_5$O$_8$ behaves as a strongly correlated paramagnet, in which Pr$^{3+}$ has a very strong tendency to form short-range-ordered magnetic clusters, although no long-range magnetic order develops.

We cannot clearly distinguish between contributions from Pr and Ni ions in our $\mu$SR experiments, and it is likely that both contribute to the $\mu$SR relaxation rates. Therefore, we cannot draw further conclusions about the microscopic details of the spin-glass formation. The lack of magnetic order may be due to a certain magnetic frustration, eventually leading to the formation of a spin glass of either Ni or Pr magnetic moments, or both. However, the relatively small difference between FC and ZFC magnetization data (with $M_{\text{sat}}$ as an upper limit, see Figs. 1 and 2) rather points to a glassy state within the Ni subsystem.

To summarize, the powder-ND and $\mu$SR measurements show no evidence for long-range magnetic order in Pr$_3$Ni$_5$O$_8$. Our magnetization data clearly demonstrate a spin-glass behavior with a freezing temperature $T_s \approx 68$ K and a distinct magnetic memory effect at all temperatures. Two magnetic processes are characterized by remarkably different relaxation rates: a slowly relaxing signal, resulting from paramagnetic fluctuations present at all temperatures, and a rapidly growing fast-relaxing signal due to the presence of short-range correlated regions in the glassy state below $T_s$. This complicated magnetic behavior may prohibit the occurrence of superconductivity in Pr$_3$Ni$_5$O$_8$. However, it is conceivable that chemical doping (i.e., a further change of the Ni valence state) suppresses the spin-glass state and eventually renders the trilayer $T'$-type nickelate Pr$_3$Ni$_5$O$_8$ superconducting [13].

This work was supported by the Swiss National Science Foundation under Grants No. 20-175554, No. 206021-163997 and No. PZ00P2-174015. This work was partly based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland.

[1] M. V. Feigel’man, V. B. Geshkenbein, and A. I. Larkin, Physica C 167, 177 (1990).
[2] B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, and J. Zaanen, Nature (London) 518, 179 (2015).
[3] J. G. Bednorz and K. A. Müller, Rev. Mod. Phys. 60, 585 (1988).
[4] J. G. Bednorz and K. A. Müller, Z. Phys. B 64, 189 (1986).
[5] Z. Kakol, J. Spalek, and J. M. Honig, Solid State Commun. 71, 283 (1989).
[6] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) 337, 345 (1989).
[7] M. A. Hayward, M. A. Green, M. J. Rosseinsky, and J. Sloan, J. Am. Chem. Soc. 121, 8843 (1999).
[8] M. Uchida, K. Ishizaka, P. Hansmann, Y. Kaneko, Y. Ishida, X. Yang, R. Kumai, A. Toschi, Y. Onose, R. Arita, K. Held, O. K. Andersen, S. Shin, and Y. Tokura, Phys. Rev. Lett. 106, 027001 (2011).
[9] V. I. Anisimov, D. Bukhvalov, and T. M. Rice, Phys. Rev. B 59, 7901 (1999).
[10] V. V. Poltavets, K. A. Lokshin, T. Egami, and M. Greenblatt, J. Am. Chem. Soc. 128, 9050 (2006).
[11] V. V. Poltavets, K. A. Lokshin, A. H. Nevidomskyy, M. Croft, T. A. Tyson, J. Hadermann, T. Egami, G. Kotliar, N. ApRoberts-Warren, A. P. Dioguardi, N. J. Curro, and M. Greenblatt, Phys. Rev. Lett. 104, 206403 (2010).
[12] J. Zhang, A. S. Botana, J. W. Freeland, D. Phelan, H. Zheng, V. Pardo, M. R. Norman, and J. F. Mitchell, Nat. Phys. 13, 864 (2017).
[13] A. S. Botana, V. Pardo, and M. R. Norman, Phys. Rev. Mater. 1, 021801 (2017).
[14] D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, and H. Y. Hwang, Nature (London) 572, 624 (2019).
[15] G. A. Sawatzky, Nat. News Views 572, 592 (2019).
[16] M. Hepting, D. Li, C. J. Jia, H. Lu, E. Paris, Y. Tseng, X. Feng, M. Osada, E. Been, Y. Hikita, Y. D. Chuang, Z. Hussain, K. J. Zhou, A. Nag, M. Garcia-Fernandez, M. Rossi, H. Y. Huang, D. J. Huang, Z. X. Shen, T. Schmitt, H. Y. Hwang, B. Moritz, J. Zaanen, T. P. Devereaux, and W. S. Lee, Nat. Mater. 19, 381 (2020).
[17] M. Crespin, P. Levitz, and L. Gatineau, J. Chem. Soc., Faraday Trans. 2 79, 1181 (1983).
[18] T. Yamamoto and H. Kageyama, Chem. Lett. 42, 946 (2013).
[19] M. A. Hayward and M. J. Rosseinsky, Solid State Sci. 5, 839 (2003).
[20] N. apRoberts-Warren, J. Crocker, A. P. Dioguardi, K. R. Shrirer, V. V. Poltavets, M. Greenblatt, P. Klavins, and N. J. Curro, Phys. Rev. B 88, 075124 (2013).
[21] O. O. Bernal, D. E. MacLaughlin, G. D. Morris, P.-C. Ho, Lei Shu, C. Tan, J. Zhang, Z. Ding, K. Huang, and V. V. Poltavets, Phys. Rev. B 100, 125142 (2019).
[22] N. Ap Roberts-Warren, A. P. Dioguardi, V. V. Poltavets, M. Greenblatt, P. Klavins, and N. J. Curro, Phys. Rev. B 83, 014402 (2011).

[23] J. Zhang, D. M. Pajerowski, A. S. Botana, H. Zheng, L. Harriger, J. Rodriguez-Rivera, J. P. C. Ruff, N. J. Schreiber, B. Wang, Y.-S. Chen, W. C. Chen, M. R. Norman, S. Rosenkranz, J. F. Mitchell, and D. Phelan, Phys. Rev. Lett. 122, 247201 (2019).

[24] J. Zhang, Y.-S. Chen, D. Phelan, H. Zheng, M. R. Norman, and J. F. Mitchell, Proc. Natl. Acad. Sci. USA 113, 8945 (2016).

[25] K. Kohayashi, H. Yamamoto, A. Nakata, I. Umehara, and M. Uehara, JJAP Conf. Proc. 6, 011106 (2017).

[26] T. Miyatake, S. Shibutani, K. Hamada, J. Gouchi, Y. Uwatoko, K. Wakiya, I. Umehara, and M. Uehara, JPS Conf. Proc. 30, 011061 (2020).

[27] S. Huangfu, G. D. Jakub, X. Zhang, O. Blacque, P. Puphal, E. Pomjakushina, F. O. von Rohr, and A. Schilling, Phys. Rev. B 101, 104104 (2020).

[28] S. Huangfu, X. Zhang, and A. Schilling, arXiv:2003.08478.

[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.102.054423 for more details about experimental methods, neutron-diffraction data, crystallographic data, and the magnetic data.

[30] H. M. Rietveld, J. Appl. Crystallogr. 2, 65 (1969).

[31] J. Rodríguez-Carvajal, Physica B 192, 55 (1993).

[32] A. Amato, H. Luetskens, K. Sedlak, A. Stoykov, R. Scheuermann, M. Elender, A. Raselli, and D. Graf, Rev. Sci. Instrum. 88, 093301 (2017).

[33] K. Jonason, E. Vincent, J. Hammann, J. P. Bouchaud, and P. Nordblad, Phys. Rev. Lett. 81, 3243 (1998).

[34] L. W. Bernardi, H. Yoshino, K. Hukushima, H. Takayama, A. Tobo, and A. Ito, Phys. Rev. Lett. 86, 720 (2001).

[35] J. N. Reimers, J. Dahn, J. Greedan, C. Stager, G. Liu, I. Davidson, and U. von Sacken, J. Solid State Chem. 102, 542 (1993).

[36] A. Chatterjee, S. Majumdar, S. Chatterjee, A.-C. Dippel, O. Gutowski, M. V. Zimmermann, and S. Giri, J. Alloy Compd. 778, 30 (2019).

[37] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).

[38] J. A. Mydosh, in Spin Glasses: An Experimental Introduction (Taylor & Francis, London, 1993).

[39] H. Vogel, Phys. Z. 22, 645 (1921).

[40] G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).

[41] S. Mukherjee, A. Garg, and R. Gupta, Appl. Phys. Lett. 100, 112904 (2012).

[42] R. Kubo and T. Toyabe, A stochastic model for low field resonance and relaxation, in Magnetic Resonance and Relaxation, edited by R. Blinc (North-Holland, Amsterdam 1967), pp. 810–823.

[43] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Phys. Rev. B 20, 850 (1979).

[44] A. Suter and B. M. Wojek, Phys. Proc. 30, 69 (2012).