Slow spin dynamics in a CoM₂O₄ A-site spinel (M=Al, Ga, and Rh)

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Abstract

We report thermomagnetic properties in magnetically frustrated A-site spinel magnets of CoAl₂O₄, CoRh₂O₄, and cluster glass CoGa₂O₄ to comprehensively show the proximity effects of the Néel-to-spin-spiral (NSS) transition, which is predicted theoretically to occur in a magnetically frustrated A-site spinel antiferromagnet. The low-temperature magnetic phase remains controversial since the magnetic state of CoAl₂O₄ is in the vicinity of the NSS transition derived by the inherent magnetic frustrated interaction for an A-site spinel magnet and is also considerably sensitive to crystallographic disorder. The antiferromagnetic and spin-glass transitions were detected by measuring the direct-current and alternating-current susceptibilities and also thermoremanent magnetization (TRM) developing below the magnetic transitions at the Néel point (Tₜ) and spin-glass transition temperature (TSG). The relaxation rate and the temperature derivative of TRM were both enhanced at Tₜ and TSG, and they decayed rapidly above and below the transitions. We succeeded in extracting the relaxation time τ and other characteristic parameters from the isothermal relaxation of TRM, which was well fitted with a non-exponential relaxation form formulated by Weron based on purely stochastic theory in order to describe the originally dielectricrelaxation. For the typical CoRh₂O₄ normal spinel (inversion-free A site) antiferromagnet and the CoGa₂O₄ random spinel spin-glass, the temperature variations of these parameters can distinguish the magnetic states. In contrast to the cases for CoRh₂O₄ and CoGa₂O₄, an enhancement of the relaxation rate of TRM for CoAl₂O₄ is indicated at low temperatures, which is probably related to the suppression of long-range antiferromagnetic order revealed by neutron diffraction studies.

1. Introduction

It is well known that thermoremanent magnetization (TRM) can create magnetic records of geomagnetic fields during the formation of rocks in the form of assemblies of ferromagnetic fine particles dispersed in a matrix consisting of paramagnetic and diamagnetic materials [1]. When the particle size is above a certain threshold and the temperature of the rock declines to below the magnetic transition temperature Tₜ, the magnetic moment of the fine particles aligns with the direction of the geomagnetic field and, at temperatures well below Tₜ, remains observable over geological time scales. At laboratory time scales, fine ferro- or ferrimagnetic particles display superparamagnetism above a certain temperature—the so-called blocking temperature TₜB [1]. The magnetic moment of the particles rotates/decays by applying magnetic activation or thermal agitation beyond an anisotropic magnetic energy KV, where K and V are the anisotropy constant and particle volume, respectively. This naïve scenario gives an estimation of the relaxation time of the magnetic moment induced by a magnetic field during cooling from T > TₜB that is, $\tau = \tau_0 \exp (KV/k_B T)$, where $\tau_0$ and $k_B$ are a characteristic relaxation time and the Boltzmann constant, respectively. TRM has been observed not only in ferromagnetic fine particles and thin films, but also in spin-glass (SG) [2, 3], antiferromagnetic fine particles [4], and bulks [5], yet it used to
In an AB$_2$O$_4$ spinel oxide, divalent and trivalent ions occupy the tetrahedral (A) and octahedral (B) sites, respectively. The A site forms a diamond lattice that consists of two penetrating face-centered cubic lattices shifted to the [111] direction of a conventional primitive lattice. Note that a diamond AF exhibits a Néel-type magnetic state for the A-site spinel antiferromagnet is suppressed not only by the frustration (J$_2$/J$_1$) but also inversion (η). In the J$_2$/J$_1$-$T$ plane, J$_2$/J$_1$ for CoAl$_2$O$_4$ was experimentally estimated to be 0.110 [15] and 0.109 [17, 18], which are close to the theoretical value of J$_2$/J$_1$ = 1/8 at the NSS boundary. The NSG boundary in CoAl$_2$O$_4$ is approximately located at η = 0.08 [15].

2. Frustration and disorder

In an AB$_2$O$_4$ spinel oxide, divalent and trivalent ions occupy the tetrahedral (A) and octahedral (B) sites, respectively. The A site forms a diamond lattice that consists of two penetrating face-centered cubic lattices shifted to the [111] direction of a conventional primitive lattice. Note that a diamond AF exhibits a Néel-type antiferromagnetic spin structure when only an exchange interaction J$_1$ is introduced between the nearest-neighbor Co ions. Because of the competition between the nearest J$_1$ and next-nearest J$_2$ interactions acting

Table 1. Magnetic parameters for CoM$_2$O$_4$ (M = Al, Rh, and Ga), magnetic transition temperature ($T_m$), effective magnetic moment ($p_{eff}$), Weiss temperature ($\theta$), and frustration parameter (f).

| Spinel       | Magnetic state | $T_m$(K) | $p_{eff}$($\mu_B$) | $\theta$(K) | $f$($-\theta/T_m$) | References |
|--------------|----------------|----------|-------------------|-------------|-------------------|------------|
| CoAl$_2$O$_4$| N              | 8.3      | 4.59              | -91         | 11                | [14]       |
| CoRh$_2$O$_4$| N              | 25       | 4.34              | -28.6       | 1.1               | [10]       |
| CoGa$_2$O$_4$| CG             | 8.2      | 4.97              | -49.3       | 6                 | [3]        |

* N and CG indicate Néel and cluster glass states, respectively.
between Co ions in the A-site, magnetic frustration is then anticipated. Microscopically, the magnetic interactions between the A-site spins $J_1$ and $J_2$ are somewhat complex and subtle [7]. The interactions are superexchange couplings mediated via several kinds of bonding A–O–B–O–A. For the A-site spinels $J_1$ and $J_2$ depend on bond lengths and bond angles in the bonding path and might be controllable, for example, by substituting a B-site cation with appropriate one with different ionic radius [8,9] and applying hydrostatic pressure [10]. Note that these interactions involve several coupling paths as depicted in [7] with extremely higher multiplicities. A Monte Carlo simulation predicts a magnetic phase diagram of the A-site spinel AF mapped on the temperature versus $J_2/J_1$ plane and a Néel-to-spin-glass (NSS) phase transition occurring at a quantum critical point (QCP) of $J_2/J_1 = 1/8$ [11]. The paramagnetic-Néel and paramagnetic-spin spiral phase boundaries meet at a Lifshitz point and penetrate below the Néel phase as an NSS boundary terminating at the critical point.

In CoAl2O4, the A-site spinels are expected to be in the vicinity of the NSS boundary and, consequently, the antiferromagnetic transition is suppressed strongly due to the magnetic frustration suggested by the frustration parameter $f = -\theta/T_m$, where $\theta$ is the Weiss temperature, which is extracted from the temperature variation of susceptibility in the paramagnetic temperature region. In contrast, for CoRh2O4, $f = 1.1$, which is quite small compared with that for CoAl2O4 (table 1), and, consequently, CoRh2O4 is seemingly categorized as a weakly frustrated AF. In actuality, magnetic neutron diffraction (ND) measurements for both magnets reveal that long-range antiferromagnetic ordering was suppressed even at $T < T_m$ for CoAl2O4; in contrast, CoRh2O4 exhibits long-range antiferromagnetic ordering below the Néel temperature $T_N = 24$ K [10,12,13]. MacDougall et al attributed the peculiar result of the magnetic ND observed in CoAl2O4 to the formation of a fragmented antiferromagnetic domain structure, since antiferromagnetic-domain wall motion seems to be kinetically inhibited below $T_m$.

Generally, for $\text{AB}_2\text{O}_4$ spinel oxides, the $\text{A}^{2+}$ and $\text{B}^{3+}$ ions distribute into both the A and B sites. The distribution is represented by the chemical formula $(\text{A}_{1-x}\text{B}_x)(\text{B}_{2-x}\text{A}_x)\text{O}_4$, where the parentheses and square brackets indicate the A-site and B-site occupancies, respectively, and $\eta$ is the so-called inversion parameter, or simply inversion. As shown in table 2, it has been indicated in cobalt spinel oxides that inversion $\eta$ distributes over the range of $0 \leq \eta \leq 0.664$. Therefore, inversion can be tuned by substituting the $\text{Al}^{3+}$ or $\text{Rh}^{3+}$ B-site cation with Ga$^{3+}$. The magnetic properties of Ga-substituted cobalt aluminate were investigated by Melot et al for CoAl2$_{1-x}$Ga$_x$O$_4$, whose inversion was tuned over the range of $0.09 \leq \eta \leq 0.63$. Similarly, Hanashima et al investigated the magnetism of quenched CoAl2O4 over the range of $0.0467 \leq \eta \leq 0.153$ [15], where they successfully tuned the inversion by changing the heat treatment temperature and indicated that an inversion-induced Néel-to-spin-glass (NSG) transition occurred around $\eta = 0.08$. This seems to be consistent with the NSG boundary of the Ga-substituted system being located between $\eta = 0.09$ and $0.36$ [9]. On the other hands, in CoRh2O4, it is hard to create inversion because of strong B-site preference of Rh$^{3+}$ [10,12].

For the case of $\eta > 0$ an inverted Co$^{2+}$ ion at the B site couples strongly with neighboring Co$^{2+}$ ions at the A site and B site via superexchange interactions mediated through bonding paths A–O–B and B–O–B, respectively. These exchange interactions distributed randomly seem to act as strong magnetic perturbations to the magnetic state for the A-site spinel magnets. In a CoGa$_2$O$_4$ random spinel with $\eta = 0.664$, far from the NSG boundary, direct current (DC) and AC susceptibility measurements revealed that a CG state appeared below $T_{CG} = 8.2$ K [3]. TRM signals the glass transition, and its time course was reproduced by a power law in the form of

$$\phi(t) = \left[1 + k(t/\tau)^\beta\right]^{-1/k}$$

for $k > 0$ and $0 < \beta < 1$, where $\tau$ is the relaxation time and $k$ and $\beta$ are macroscopic mathematical parameters representing ‘interaction’ and fractal geometry, respectively [6]. Remarkably, the so-called interaction parameter $k$ is related to the collective nature of the interaction and is associated with the non-extensive parameter $q$ via a simple equation, $k = (q-1)/(2-q)$ [19]. The parameter $q$ appears in Tsallis’ generalized non-extensive entropy:

$$S_q = k_0 \int_0^\infty \frac{p^q(x)}{1 - q} dx,$$

where $p(x)$ is a distribution function with respect to $x$, with the latter being a correlation length in a magnetically interacted spin system. The temperature dependence of $q$ obtained from the TRM relaxation curve of CoGa$_2$O$_4$

| Spinel      | $a$ (Å) | $\eta$ | References |
|-------------|---------|--------|------------|
| CoAl$_2$O$_4$ | 8.1030  | 0.2646 | 0.055 [14] |
| CoRh$_2$O$_4$ | 8.50068(1) | 0.26087(4) | 0.060(1) [10] |
| CoGa$_2$O$_4$ | 8.32654(1) | 0.2584(1) | 0.664(8) [3] |

Table 2. Crystallographic parameters for the CoM$_2$O$_4$ cubic spinels (M = Al, Rh, and Ga).
is consistent with the theoretical findings for complex systems [3] and experimental results for metallic spin-glass systems [2]: that is, (i) $q$ approaching 2 at $T \ll T_{SG}$, (ii) $q = 5/3$ at the SG transition, and (iii) $q(T) = 0$ asymptotically at $T \gg T_{SG}$.

We present in this article a comparison between slow spin dynamics in a lightly inverted CoAl$_2$O$_4$ A-site AF and a weakly frustrated AF state in CoRh$_2$O$_4$, as well as in the CG state in CoGa$_2$O$_4$. For the end numbers, the magnetic and crystallographic properties of the samples are summarized in tables 1 and 2.

3. Experimental

Samples of the end numbers examined in this work were the same as those whose structural, magnetic, and thermal properties were examined previously [3, 10, 14], as listed partly in tables 1 and 2. The DC and AC magnetizations were measured using the Magnetic Properties Measurement System (MPMS-XL; Quantum Design). The extrinsic components in the real and imaginary parts of AC susceptibility, which are significant at frequencies above 300 Hz, were corrected by referring to those measured for a diamagnetic reference material paraffin. Specific heat was measured using the Physical Properties Measurement System (PPMS Dynacool; Quantum Design). The temperature dependence and relaxation of TRM were measured after field cooling with an excitation DC field of $H_{FC} = 100$ Oe applied at $T = 70$ K. After the measurement temperature, $T = T_{M}$, had been reached, the sample was held at that temperature for $t_{m} = 300$ s. The magnetic field was then immediately reduced to zero. An extrinsic contribution of $\chi(T_M)H_{res}$ produced by the residual field $H_{res}$ was corrected. After each isothermal relaxation measurement, $H_{res}$ was estimated by measuring the residual magnetization $\chi(T)H_{res}$ in the paramagnetic region at $T = 70$ K, where the short-range magnetic order was diminished [14].
First presented are magnetic transitions and magnetic properties for the end numbers of the CoAl$_2$O$_4$, CoRh$_2$O$_4$, and CoGa$_2$O$_4$ A-site spinel cobalt magnets; as shown in figure 1 and table 1, these magnets plausibly can be categorized as a frustrated AF located in the vicinity of the NSS boundary at $J_2/J_1 = 1/8$, a weakly frustrated AF with $J_2/J_1 \approx 1/8$, and a CG, respectively. Figure 2 shows magnetic susceptibility after zero field-cooled (ZFC) pretreatment and field-cooled pretreatment (FC) with $H_{FC} = 100$ Oe and thermoremanent magnetization ($M_{TR}$). The divergence between the ZFC and FC susceptibilities are indicated at $T = T_m$ concomitantly with emerging TRM for both CoRh$_2$O$_4$ and CoAl$_2$O$_4$. Indeed, magnetic transition temperatures can be identified precisely by the sharp minima in the temperature derivatives of $M_{TR}$ and $\chi$ ($ZFC$), whose anomalous positions coincide with that of magnetic component of specific heat $\Delta C_{mol}/T$ to within $\pm 0.5$ K (figures 3(a)–(d)). In CoGa$_2$O$_4$, the CG transition was indicated in the aforementioned quantities in addition to the relaxation rate of $\Delta C_{mol}/T$ and $\Delta M_{mol}/T$ are taken from [18] and [14] for CoRh$_2$O$_4$ and CoAl$_2$O$_4$, respectively.

4. Results and discussion

In a diluted limit far from the NSG boundary, a nearly isolated magnetic cluster created by inverted Co ions at the B site is embedded in the antiferromagnetic matrix. The magnetic deformation due to inversion is screened by the spin-spiral matrix and expected to be confined within the order of the CoAl$_2$O$_4$ unit cell length [20]. This scenario might be applicable for the AF magnet, and likewise for CoAl$_2$O$_4$ in the vicinity of the NSS boundary; this might give a microscopic picture of the cluster formation in the A-site AF magnets. A quenched magnetic moment is induced below $T_m$ by field cooling under an excitation field $H_{FC}$ (figure 4(a)). Through interactions with the surrounding AF matrix, the TRM of the magnetic cluster appreciably signals a magnetic transition of the AF matrix. As shown in figure 4(b), the temperature dependence of $M_{TR}(T)$ does not correspond with that of magnetic peak intensity in the ND $I(T)$ previously reported for CoAl$_2$O$_4$ with $\eta = 0.05$ [21]; consequently, we attribute this lack of correspondence to the coherent magnetic contribution most likely due to the inverted Co$^{2+}$ spins distributed randomly in the B site. The $M_{TR}(T)$ curve follows the single exponent power function $\phi(T) = \phi_0(1–T/T_m)^\alpha$ with $\alpha = 0.82$, whereas $\alpha = 0.51$ for the case of $\phi(T) = I(T)$ (figure 4(b)). Additionally, the $M_{TR}(T)$ curve shows an upturn at low temperatures, which is enhanced at a high $H_{FC}$ (figure 4(c)).

Figure 3. The temperature derivatives of TRM and ZFC susceptibility for CoRh$_2$O$_4$ (a) and CoAl$_2$O$_4$ (c). The magnetic component of specific heat $\Delta C_{mol}/T$ as a function of temperature for CoRh$_2$O$_4$ (b) and CoAl$_2$O$_4$ (d). Vertical dashed lines represent the positions of magnetic transition temperatures $T_m = 25$ K for CoRh$_2$O$_4$ and $= 8.5$ K for CoAl$_2$O$_4$. The temperature variations of $d\chi_{mol}/dT$ and $\Delta C_{mol}/T$ are taken from [18] and [14] for CoRh$_2$O$_4$ and CoAl$_2$O$_4$, respectively.
In contrast, the weakly frustrated CoRh$_2$O$_4$ undergoes an antiferromagnetic ordering below $T_N = 25.0(2)$ K; concomitantly, TRM shows typical temperature variation for an order parameter of a spin system, such as those of Ising and Heisenberg models (figure 5(a)). Indeed, for CoRh$_2$O$_4$, $I(T)$ detected by the ND measurement shows a temperature variation following a single exponent power function with $\alpha = 0.5$ and 0.68 for the Ising

**Figure 4.** (a) Temperature variations of $M_{\text{TR}}$ measured after field cooling under various magnetic field strengths $H_{\text{FC}}$ for CoAl$_2$O$_4$. Solid lines represent the fitting curves using $\phi(T) = \phi_0(1 - T/T_m)^\alpha$. (b) Temperature dependence of $M_{\text{TR}}(T)$ and the integrated intensity of the magnetic peak detected by neutron diffraction (ND) [21]. (c) Temperature derivatives of $M_{\text{TR}}$ as a function of temperature. The value of $dM_{\text{TR}}/dT$ is scaled by the scale factors (SFs) shown in the plot.
Figure 5. (a) Temperature variations of $M_{TR}$ measured after field cooling under various magnetic field strengths $H_{FC}$ for CoRh$_2$O$_4$. The magnetic peak intensity of neutron diffraction (ND) is also shown [12]. Solid lines represent the fitting curves using the single exponent form $\phi(T) = \phi_0 (1 - T/T_N)^\alpha$. (b) $M_{TR}(2\,K)$ and the exponent $\alpha$ as a function of $H_{FC}$ obtained by a numerical fitting of the $M_{TR}(T)$ curve and the intensity-temperature curve of the magnetic peak [12]. (c) Temperature derivatives of $M_{TR}$ as a function of temperature. The value of $dM_{TR}/dT$ is scaled by the scale factors (SFs) shown in the plot.
and Heisenberg models, respectively [12]. Interestingly, $M_{TR}(T)$ curves measured after field cooling with various fields could be reproduced by this function with an exponent of $\alpha = 0.39 - 0.48$ (figure 5(b)). While $\alpha$ seems to depend slightly on $H_{FC}$, as shown in figure 5(b), under weak fields ($H_{FC} \leq 10$ kOe), the exponent stays at $\alpha = 0.41 \pm 0.02$. This value corresponds well to $\alpha = 0.46$, as obtained from the temperature dependence of magnetic peak intensity observed in ND measurements [12], which is extracted by a numerical fitting with the single exponent power function $\phi(T)$. This implies that $M_{TR}$ directly reflects the sublattice magnetization developed below $T_N$ for CoRh$_2$O$_4$. Most likely, an uncompensated spin component due to off-stoichiometry and/or structural defects bring about TRM. Actually, the temperature derivative of $M_{TR}$ shows a sharp peak at $T = T_N$, and the $dM_{TR}/dT$ curves at various excitation fields collapse into a universal curve when one uses appropriate scale factors for the respective curves (figure 5(c)). The entity resulting in the appearance of TRM for CoRh$_2$O$_4$ does not considerably perturb the Néel state below $T_N$ and, as expected, acts as a locally situated magnetic probe. Figure 6 shows the temperature variations of $M_{TR}$ and $dM_{TR}/dT$ at various activation fields for CoGa$_2$O$_4$. The $M_{TR}(T)$ curve activated during the field cooling under $H_{FC} = 100$ Oe is reproduced by $\phi(T)$ with $T_m = 8.2$ and $\alpha = 0.77$ [3]. The value of exponent $\alpha = 0.77$ is comparable with that for CoAl$_2$O$_4$. Note that $M_{TR}(T)$ exhibits an upturn with decreasing temperature, consequently, as indicated in CoAl$_2$O$_4$, a stepwise variation of the $dM_{TR}/dT$ curve is indicated (figure 6(b)), whereas the value of $M_{TR}$ of CoGa$_2$O$_4$ is considerably larger than that of CoAl$_2$O$_4$. 

Figure 6. (a) Temperature variations of $M_{TR}$ measured after field cooling under various magnetic field strengths $H_{FC}$ for CoGa$_2$O$_4$. $M_{TR}(T)$ at $H_{FC} = 0.1$ kOe and the calculated curve (solid line) are taken from [3]. (b) Temperature derivatives of $M_{TR}$ as a function of temperature. The values of $M_{TR}$ and $dM_{TR}/dT$ under $H_{FC} = 100$ Oe are magnified by SF = 15 in order to compare with those under $H_{FC} = 5$ kOe.
Figures 7 (a) and (b) show isothermal TRM relaxation curves for CoRh$_2$O$_4$ and CoAl$_2$O$_4$, respectively, measured well below $T_m$. As seen for CoGa$_2$O$_4$ [3], the decay curves are reproduced by Weron’s generalized probabilistic relaxation function (hereafter simply denoted as the Weron function) [6]:

$$\phi_W(t) = \left[ 1 + k \left( \frac{t}{\tau} \right)^\beta \right]^{-1/k},$$

where $k$ is an interaction parameter and related to the waiting time, and $\beta$ is related to the fractal geometry and the dynamic nature of the relaxation dynamics [19]. This form asymptotically corresponds to a stretched exponential and logarithmic at the limits of $k \rightarrow 0$ and $\infty$, respectively. Note that a Debye decay function $f_D(t) = \exp\left[-(t/\tau)\right]$ is recovered when $k = 0$ and $\beta = 1$. As extracted from the decay curves of TRM while assuming $\beta = 0.6$ [2, 3], the parameters $\tau$ and $k$, as displayed in figure 8, are compared with those previously reported for CG CoGa$_2$O$_4$ [3]. For the weakly frustrated AF, $\tau$ seemingly depends on temperature, following an Arrhenius-type variation with an activation energy $E_a/k_B$ roughly corresponding to $T_N$; similar to the case of CoGa$_2$O$_4$, while in the vicinity of the transition, $\tau$ is slightly enhanced, where a critical slow-down is expected to occur. The enhancement of $1/\tau$ at slightly below $T_m$ is observed also in CoAl$_2$O$_4$. In CoAl$_2$O$_4$, remarkably, at $T < T_m$, $1/\tau$ increases with decreasing temperature. The low-temperature enhancement of $1/\tau$ is in contrast with the trends seen in CoRh$_2$O$_4$ and CoGa$_2$O$_4$. Thus, for the AF magnets, the interaction parameter $k$ is quite large compared with that of the CoGa$_2$O$_4$ CG system, which shows a significant temperature dependence. Figure 9 shows temperature variations of the real and imaginary components of AC susceptibility measured at various frequencies for CoRh$_2$O$_4$ and CoAl$_2$O$_4$. The negative value in $\chi''(T)$ results from the correction of the background signal which was not negligible at higher frequencies above 300 Hz. In contrast with the aforementioned findings for TRM, we emphasize that no frequency variations were detected in the range of $0.3 \leq \nu \leq 1500$ Hz, which is consistent with previous reports for CoAl$_2$O$_4$ with $\eta < 0.08$ [15]. We note, therefore, that discrepancies of a dynamic nature below the transition between the A-site spinel magnets were remarkable at $\tau > 10^4$ s (correspondingly $\nu < 10^{-4}$ Hz).

Especially, in CoAl$_2$O$_4$, whose magnetic ground state remains controversial, comprehensive TRM study is needed to reveal the effect of disorder on magnetism in addition to other macroscopic quantities: indeed, the temperature variation of TRM depends strongly on the magnitude of $H_{FC}$, and there is an upturn in the $M_{TR}(T)$ curve enhanced with increasing $H_{FC}$ (figures 4(a) and (c)). Note that the magnetic state of CoAl$_2$O$_4$, which is located in the vicinity of the NSG and NSS boundaries, is dependent on its magnetothermal history and,
therefore, can be characterized plausibly by the stochastic parameters $k$ and $\beta$, in addition to $\tau$ extracted from TRM relaxation. By comparison with those for CoRh$_2$O$_4$, we deduce that these magnetothermal-history and chemical-disorder (inversion) effects exhibited in CoAl$_2$O$_4$ reflect the proximity to the NSS QCP, where spin fluctuation is generally enhanced [16–18]. As indicated by MacDougall et al that the fragmented antiferromagnetic domain structure is retained even well below $T_m$ [16] is possibly detected by the magnetothermal quantities. The domain structure in CoAl$_2$O$_4$ is somewhat similar phenomenologically to the aggregated nanocrystals of a Co$_3$O$_4$ A-site spinel AF exhibiting both antiferromagnetic and glassy transitions at 32 and 10 K, respectively, with remarkable magnetothermal behaviors developing below the transitions [4]. In order to clarify mechanism of the suppression of long-range order, we need to investigate the lattice volume effect on the magnetic state to approach the QCP of the NSS ($J_2/J_1 = 1/8$) in chemically substituted systems such as CoAl$_{2-x}$Rh$_x$O$_4$ and, concomitantly, the inversion effect on chemically substituted systems such as CoAl$_{2-x}$Ga$_x$O$_4$ for precisely controlling inversion in the vicinity of the NSG boundary.

Figure 8. Relaxation time $\tau$ as a function of $T_m/T$ ($m = N$ or SG) (a) and interaction parameter $k$ as a function of reduced temperature $T/T_m$ (b) extracted from the isothermal TRM relaxation curves for the antiferromagnetic A-site spinel oxides. Dashed curves represent those obtained previously for CoGa$_2$O$_4$ [3].
Finally, let us comment on the structure in $\frac{dM_{TR}}{dT}$ for CoAl$_2$O$_4$ and CoGa$_2$O$_4$ (figures 4(c) and 6(b)). In the CG state for $M =$ Ga, the spikes are indicated at $T = 4$ and 3 K even at the lowest field of $H_{FC} =$ 100 Oe and are enhanced with increasing $H_{FC}$. This structure in $\frac{dM_{TR}}{dT}$ is observable more significantly for CoAl$_2$O$_4$ above 1 kOe. Note that, in contrast, for CoRh$_2$O$_4$ $\frac{dM_{TR}}{dT}$ does not show any significant structures up to $H_{FC} =$ 20 kOe as shown in figure 5(c). Therefore, it is plausible that the origin of the structure is related with the magnetic cluster located around inverted Co$^{2+}$ spins. The inverted spin is distributed randomly into the B-site and acts as quenched disorder introduced into the magnetically frustrated A-site spinel. The theoretical investigations have predicted that the disorder lifts the degeneracy due to the frustration and stimulates an ordering transition [20]. The existence of the structure in $\frac{dM_{TR}}{dT}$ might indicate a multistageous magnetic transition below $T_N$ and $T_{SG}$ for CoAl$_2$O$_4$ and CoGa$_2$O$_4$, respectively. Further investigation is needed to clarify the origin of the structure below the transition.

5. Conclusion

In this study, we revealed that in frustrated antiferromagnetic materials, regardless of whether the degree of frustration was high or low, or whether the magnetic ground state was of a long-range ordered spin system or a glassy state, TRM sensitively signals the magnetic transition and slows magnetic dynamics. The transition temperature can be detected precisely and corresponds with that detected by susceptibility and specific heat within an error of $\pm 0.5$ K. The relaxation analysis using Weron’s generalized probabilistic function shows that...
magnetic ground states of A-site AFs can be distinguishable from those of CoGa$_2$O$_4$ CG. The temperature variations of relaxation time and the macroscopic probabilistic mathematical parameter are also distinguishable among the spinel AFs examined in this and previous works [3]. Both in the weakly frustrated CoRh$_2$O$_4$ AF and the CoGa$_2$O$_4$ CG, the temperature variation of relaxation time follows an Arrhenius law $\tau = \tau_0 \exp(E_a/k_B T)$ below the magnetic transition with an activation energy $E_a$ comparable with the transition temperature ($k_B T_N$ or $k_B T_{SC}$), whereas in strongly frustrated CoAl$_2$O$_4$, relaxation time decreases with decreasing temperature. Although the microscopic origin of TRM in these AFs remains unclarified, TRM results from magnetic clusters embedded in the antiferromagnetic matrix and both the static and dynamic natures of the materials seem to provide unique information for the antiferromagnetic matrix.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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