Correlation, excitation, and relaxation of the antiferromagnetic nanoparticle

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We study the dynamics of spins in the canted antiferromagnetic hematite nanoparticles α-Fe₂O₃. The system includes an antiferromagnetic exchange \( J \) between two sublattices as well as the potential dominated by a uniaxial anisotropy and dissipates through the thermally triggered spin-phonon mechanism. The exchange \( J \) is found to reduce the superparamagnetic relaxation and drive the incoherent relaxation of transverse spins in the low temperature. Dynamical properties are semi-quantitatively understood within a role of the exchange interaction \( J \) and agree well with recent inelastic neutron scattering experiments.

Magnetic properties of the fine particles of a size \( \sim O(10) \) nm are interesting and currently attracting much attention. In the system, the most relevant energy scale tends to be the magnetic anisotropy energy, easily comparable to the thermal energy \( T \), so that the magnetization (or superspin) is subject to considerable thermal fluctuation, called the superparamagnetic relaxation\[1\]. Phenomena of such magnetic fluctuations have the potential importance in the fundamental research as well as the technological application\[2\].

Hematite, \( \alpha-Fe_2O_3 \), is a mineral of the corundum (rhombohedral) structure at room temperature, characterized by the rhombohedral axis [111] and the basal (111) plane. Spins in hematite are slightly canted away from antiferromagnetic (AFM) orientation on the basal plane, giving place to the weakly ferromagnetic (FM) state, between the Morin temperature \( T_M \approx 260 \) K and the Néel temperature \( T_N \approx 956 \) K, but spins are oriented along the [111] axis and perfectly antiferromagnetic below \( T_M \). Magnetic properties are found to depend on the particle size and \( T_M \) is less than 5 K in typical nanoparticulate hematites\[3\], where several kinds of magnetic anisotropy energies, not present or much smaller in the bulk, play important roles. In nanoparticulate hematites, the magnetization oscillates due to superparamagnetic relaxation along the easy axis and collective magnetic excitations in vicinity of the easy axis\[2\].

Many studies of the magnetic fluctuations in the nanoparticulate hematite are carried out using Mössbauer spectroscopy or measuring the magnetic susceptibility. Morup and his coworkers have used Mössbauer spectroscopy and studied the energy scale of the superparamagnetic relaxation and anisotropic barrier\[4\]. They have also explored effects of the inter-particle interaction in strongly interacting nanoparticles (e.g., uncoated dry particles or a form of mixture such as \( \alpha-Fe_2O_3+CoO \) or \( ^{57}Fe-NiO+CoO \)) and found the absence of fast superparamagnetic relaxation, i.e. the slowing down of the relaxation\[5\]. By the way, the magnetic relaxations in the system are argued to occur highly fast, being almost the ultrafast process (in the time scale of \( \lesssim O(10^{-12}) \) seconds or in the frequency scale of THz range), and the Mössbauer spectroscopy or susceptibility measurements are then found to be slow probes for the relevant magnetic dynamics. By the same group and coworkers, due to those reasons, the inelastic neutron scattering experiment is suggested as one of valuable complements\[6\].

In this paper, we investigate the detailed dynamics of the magnetization in the AFM nanoparticle system. The system incorporates the AFM exchange \( J \) between two sublattices as well as the potential by the anisotropy and undergoes the spin-relaxation through the spin-phonon mechanism. A main goal of the paper is to understand the respective dynamics and relaxation of both the superparamagnetic fluctuations and the collective magnetic excitations with respect to the temperature \( T \). Prior to the present work, theoretical studies have analytically shown that the superparamagnetic relaxation follows the simple Arrhenius behavior of \( \sim \Gamma_0(T)e^{-E_B/T} \) with a certain form of \( \Gamma_0(T) \), where \( E_B \) the energy barrier, for FM grains (like Mn₁₂O₁₂ molecules)\[7,8\]. At the very low temperatures \( (T \lesssim 2 \) K), however, it is found that the relaxation deviates from the Arrhenius law and is dominated by a resonant tunneling between low-lying states\[9,10\]. In the present work, such low temperature regimes are not assumed.

Considering that spins in the bulk hematite are in the slightly canted AFM (or weakly FM) state on the (111) basal plane, where the hexagonal crystal anisotropy is expected to be the largest energy scale, \( J_z \) is noted to be a natural choice (\( J_z \)) of two AFM sublattices, with a size of \( S \gg 1 \), and \( K_z \) and \( K_y \) are uniaxial anisotropic constants along \( \hat{z} \) ([111] direction) and in the basal plane, respectively, and \( J \) is the exchange between two sublattice magnetizations. \( K_z \) is expected to be the largest energy scale, i.e., \( K_z \gg K_y \), and \( K_z \gg J \). \( K_z S^2 \) is noted to be a natural energy unit. \( \mathcal{H}_0 \) can be easily diagonalized by taking the basis of \( |S_{1z},S_{2z}\rangle \) and performing the calculation of Clebsch-Gordan coefficients for the coupling term. In addition to \( \mathcal{H}_0 \), we consider the spin-phonon interaction \( \mathcal{V} \) (\( = \mathcal{V}_1+\mathcal{V}_2 \)) raising the spin-relaxation, \( \mathcal{V}_i = v_i f \),

\[
  v_i = g_0(S_{1z}S_{1z} + S_{1y}S_{1y}) + g_1S_{1z}S_{1y} + h.c.,
\]

where \( f \) denotes the lattice deformation. The first term in Eq. (2) gives rise to transitions from \( |m_i\rangle \) to \( |m_i \pm 1\rangle \), while the second term leads to transitions to \( |m_i \pm 2\rangle \).
We have interests in the relaxational dynamics of spins at the AFM Bragg scattering, which is given by the following correlation function, $S_\mu = S_{1\mu} - S_{2\mu}$, $\mu = x, y, z$.

$$\phi_{\mu\mu}(\tau) = \langle S_\mu(\tau)S_\mu \rangle = \langle S_\mu e^{-iL_\tau}S_\mu \rangle,$$

(3)

where $L$ is the Liouville operator, $L\mathcal{O} = [\mathcal{H}, \mathcal{O}]$, $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$. It is the spectral function $J_{\mu\mu}(\omega) = \int d\tau e^{i\omega\tau} \phi_{\mu\mu}(\tau)$ that can be compared directly with the inelastic neutron scattering experiment. Up to the second order of $\mathcal{V}$, the correlation function $\phi_{\mu\mu}(\tau)$ is written as $\phi_{\mu\mu}(\tau) = \langle e^{i\beta E_\tau}S_\mu e^{-i\beta E_\tau}e^{-iL_\tau}S_\mu \rangle$, which is valid to the lowest order in the memory function. By introducing the relaxation matrix $R$ whose elements consist of the transition probabilities of the Markov equation, we replace $e^{-iL_\tau}$ by $e^{-R_\tau}$

$$\phi_{\mu\mu}(\tau) = \langle e^{i\beta E_\tau}S_\mu e^{-i\beta E_\tau}e^{-R_\tau}S_\mu \rangle.$$

(4)

With the basis of the eigenstate of $\mathcal{H}_0$, elements of the relaxation matrix $R$ are found as follows: $R_{nm} = \sum_{n=1}^{\mathcal{N}} \gamma_{n\rightarrow m} + \sum_{m=0}^{n-1} \gamma_{n\rightarrow m}$, and $R_{mn} = -\gamma_{m\rightarrow n}$ for $n > m$, and $R_{nm} = e^{-E_n/E_m}/T\gamma_{n\rightarrow m}$ for $n < m$, where $\mathcal{N} = (2S + 1)^2$ is the dimension of the matrix and finally $\gamma_{n\rightarrow m}$ is defined by $\mathcal{N}$.

$\gamma_{n\rightarrow m} = \alpha \frac{|\langle n|m \rangle|^2}{1 - e^{-E_n-E_m}/T}(E_n - E_m)^3$.

We assume $E_n > E_m$ for $n < m$. $R$ is in fact a generalization of Orbach’s process to a spin cascade. For a coupling to elastic waves, $\gamma_{n\rightarrow m}$ should be $\propto (E_n - E_m)^3$ from the line shape function. It should be noted that the eigenstate of the relaxation matrix $R$ does not construct an orthonormal basis set because $R$ is not a (real) symmetric matrix. We then need an orthogonalization process of nonorthogonal basis, i.e. like the Gram-Schmidt orthogonalization. Putting the eigenstate of $R$ with the relaxation eigenvalue of $\lambda_i$ as $|p_i\rangle$, the orthogonalized state $|\varphi_j\rangle$ is $|\varphi_j\rangle = |p_j\rangle - \sum_{i=0}^{i-1} C_i^{j} |p_i\rangle |\varphi_i\rangle$ for $i < j$. Now the correlation function of $\phi_{\mu\mu}(\tau)$ is expressed as

$$\phi_{\mu\mu}(\tau) = \sum_n \sum_n e^{-\beta E_n} e^{i(E_n - E_m)/T} \langle m|p_i\rangle |\varphi_j\rangle$$

(5)

$$\times \sum_{j=0}^{j-1} C_j^{i} e^{-\lambda_j\tau} \langle m|p_i\rangle |\varphi_j\rangle |S_\mu|n \rangle.$$
K_z S^2$, but the excitation energy \( \omega \) (also \( \Delta_y \) and \( \Delta_z \) given later) should be scaled by \( 2K_z S \) rather than \( K_z S^2 \) from \( K_z S^2 - K_z (S - 1)^2 \approx 2K_z S \). At low temperatures (\( T \ll K_z S^2 \)), there are two distinctly different types of dynamics, namely the superparamagnetic fluctuation \( J_\parallel(\omega) = J_{xy}(\omega) \) and the collective magnetic excitation \( J_\perp(\omega) = J_{yy}(\omega) + J_{zz}(\omega) \).

Collective magnetic excitations lead to the inelastic scattering process. The relative intensity of \( J_{yy}(\omega) \) and \( J_{zz}(\omega) \) depends on the ratio of two different spin-dissipation channels in Eq. (2). We take the ratio \( g_1/g_0 = 0.5 \) because transitions of \( \delta m_i = 1 \) are considered to occur more probably than \( \delta m_i = 2 \) and \( g_0^2 = 1 \times 10^{-3} \). Under the ratio, it is found that \( J_\perp(\omega) \) is governed by \( J_{yy}(\omega) \) and \( J_\perp(\omega) \approx J_{yy}(\omega) \). For three sets of parameters, we provide the spectral functions in Fig(\text{2}). We note that two important features characteristically develop with respect to \( \xi, \zeta \), and \( T \): one is the collective excitation energy and the other is the relaxation of spins. By comparing panels in Fig(\text{2}), it is found that the excitation energies of \( S_y(\Delta_y) \) and \( S_z(\Delta_z) \) behave differently. In Fig(\text{3}), the collective excitation energies for \( \xi \) and \( \zeta \) are given. We find that \( \Delta_y (\approx \Delta_z) \) is scaled roughly by \( \sim \sqrt{\xi(\xi + \zeta)} \), that is, \( \Delta_y \propto \sqrt{\xi} \) for \( \xi \ll \zeta \) and \( \Delta_y \propto \xi \) for \( \zeta \sim 0 \). This is consistent with the result of inelastic mode energy of a pure antiferromagnet \[ \text{(2)} \] \[ \text{(3)} \]. On the other hand, \( \Delta_z \) is by \( \sim \sqrt{\xi + \zeta} \). Especially, by the symmetry, for a case of \( \xi = 1 \), \( \Delta_y \) should be same as \( \Delta_z \), \( \Delta_y = \Delta_z \approx \sqrt{\xi + 1} \), while, for \( \xi \to 0 \), \( \Delta_y \) goes to 0 by \( J_{yy}(\omega) = J_{zz}(\omega) \). Now, let us consider the relaxation of the longitudinal and transverse components of spins, which is in principle understood from the broadness of curves in Fig(\text{2}). Instead of directly measuring the broadness, however, for the systematic investigation of the relaxation, we define and propose a useful renormalized dissipation parameter \( \gamma_{nm}^\mu \); \( \sum_j \sum_{i=0}^j C_j e^{-\lambda_\mu \tau} \langle m|p_i|\langle \varphi_j|S_\mu|n \rangle \approx e^{-\gamma_{nm}^\mu \tau} \langle m|S_\mu|n \rangle \), where \( \gamma_{nm}^\mu \) is found to describe the relaxation of the system at least in an approximate sense. It is evident that the relaxation of the system is mainly governed by some smallest eigenvalues of \( \lambda_i \)'s and it is then essential to account for the long-time behavior after long enough \( \tau \) has elapsed. Due to the reason, we obtain \( \gamma_{nm}^\mu \) by integrating both sides from \( \tau = 0 \) to \( \tau = \infty \); \( \gamma_{nm}^\mu \approx \langle m|S_\mu|n \rangle \left[ \sum_j \sum_{i=0}^j C_j \langle m|p_i|\langle \varphi_j|S_\mu|n \rangle \right] \left/ (\lambda_i + \delta) \right. \), where the finite dissipation \( \delta = 2.5 \times 10^{-3} K_z S^2 \) has been added for the stable calculation. \( \delta \) can be understood corresponding to the finite energy resolution in an actual experiment \[ \text{(4)} \]. With \( \gamma_{nm}^\mu \), the time-dependent spectral function \( \phi_{\mu\mu}(\tau) \) is \( \phi_{\mu\mu}(\tau) = \sum_n \sum_{m} e^{-\beta E_m e^{i(E_m - E_{\mu} + \gamma_{nm}^\mu \tau)}} |\langle n|S_\mu|m \rangle|^2 \), from which \( \gamma_{\mu} \) is further defined as the smallest value of \( \gamma_{nm}^\mu \) at the peak position of the spectral function of \( S_\mu \). Behaviors of \( \gamma_{\mu}(T) \) have essential importances in that the magnetic relaxation of spins and related dynamics of energy dissipation can be well understood through them. We have two distinguishable kinds of the spin relaxation, as shown in Fig(\text{4})): one is the superparamagnetic relaxation along the easy axis \( \gamma_\perp(T) \); Figs(\text{4}a) and (c)) and the other is the relaxation by the collective excitations transverse to the easy axis \( \gamma_\parallel(T) \) (Figs(\text{4}b) and (d)). Because \( \gamma_\perp(T) \) is always larger than \( \gamma_\parallel(T) \), consistent with \( J_{yy}(\omega) \gg J_{zz}(\omega) \), it is reasonable to put \( \gamma_\parallel(T) = \gamma_\parallel(T) \). Like cases of FM grains, the superparamagnetic relaxation still follows the simple Arhenius behavior as a first approximation, even if the relaxation has two-dimensional nature. However, the energy barrier depends on \( \xi \) and \( \zeta \) and does not have so simple a form.
From Fig.4(a), it is evident that the AFM exchange $J$ reduces the superparamagnetic relaxation, in other words, the energy barrier increases with $J$ as shown in Fig.4(e). This finding is consistent with the claim of the absence of the fast superparamagnetic relaxation in the interacting nanoparticles through the Mössbauer spectroscopy. Without the exchange, the energy barrier approximately follows $\sim K_\parallel S^2$, which implies $\gamma_x \propto e^{-T/\xi}$; $\gamma_x \propto e^{-0.46/T}$ for $\xi = 0.5$ and $\zeta = 0$. Figures 4(b) and (d) give the transverse relaxation, quite different from the superparamagnetic relaxation. In the low temperatures, to increase the temperature reduces $\gamma_\perp(T)$. $\gamma_\perp(T)$ has then a minimum and slowly increases with $T$. In such a sense, the transverse responses of spins are found incoherent in the low temperatures. We conclude that the incoherence is driven by the AFM spin exchange $J$ because $\gamma_\perp(T)$ is always coherent for $J = 0$ (a thick line in Fig.4(b)). The incoherent behaviors of $\gamma_\perp(T)$ in the low temperatures has been actually observed in the inelastic neutron scattering experiment for $\alpha$-Fe$_2$O$_3$.[4]

Here we can estimate the system parameters $K_\parallel S^2$, $K_\perp S^2$, and $JS^2$ from the scaled dynamical quantities.[17] Their estimates have been done with appreciable error ranges from temperature fits in various ways by Morup and his coworkers.[5] A typical one of them is $K_\parallel S^2 \sim 500$ K (i.e. $\sim 42$ meV) from Arrhenius behavior of the superparamagnetic relaxation, but it is found from Fig.4(e) that the value may have been overestimated almost by 60%. Thus, we estimate $K_\parallel S^2 \sim 300$ K ($\sim 25$ meV), while the value of $K_\perp S^2$ is more uncertain because its value is not known for the nanoscopic system, but of a same order of magnitude with the bulk case. So we take $K_\perp S^2 \sim 1000$ K ($\sim 83$ meV), that is, we have $\xi = 0.3$. On the other hand, the unit excitation energy $2K_\perp S$ can be found $\sim 0.5$ meV to be consistent with the experiment. The inelastic energy mode ($\Delta_\perp$) is then $\sim 0.3$ meV at $T = 0.1$ ($\sim 100$ K). The value of $JS^2$ can be estimated as 300-500 K from the transverse excitation energy $\Delta_\perp$ in Fig.4 and from the relaxational behaviors of spins in Fig.4. Based on the estimations, $\gamma_\perp(T)$ is about $\mathcal{O}(10^{-3})$ meV and $\gamma_\perp(T)$ about $\mathcal{O}(10^{-1})$ meV in the temperatures $T \lesssim 0.2$ (i.e. $T \lesssim 200$ K). We note $\gamma_\perp(T)$ is larger than $\gamma_x(T)$ by $\mathcal{O}(10^2)$, which is consistent with the actual situation of the experiment.[6]

In summary, we have investigated the dynamics of spins in the antiferromagnetic hematite nanoparticle $\alpha$-Fe$_2$O$_3$ with the explicit AFM exchange $J$. The exchange $J$ has been found to reduce the superparamagnetic relaxation and also induce the incoherent oscillation of transverse spins in the low temperature. The spin responses are well understood within the model and a semi-quantitative estimation of the relevant parameters has been done through a comparison with the recent inelastic neutron scattering experiments.

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[16] By our estimation ($K_\parallel S^2 \sim 83$ meV), a finite dissipation (or broadness) $\delta = 2.5 \times 10^{-4}$ is corresponding to $\sim 20$ $\mu$eV, which is the same order of the energy resolution adopted in Ref. 4.
[17] From estimated $K_\parallel S^2$ and $2K_\perp S$, $S \sim \mathcal{O}(10^2)$ is easily found. But actual evaluations are done for a smaller $S = 10$ ($N = 441$) due to practical limitations. Nevertheless, thanks to scaling behaviors (all the relevant quantities are scaled by either $K_\parallel S^2$ or $2K_\perp S$; that is, results of Figs.4(b) hardly depend on a value of $S(\gtrsim 10)$ except for the absolute intensity of the spectra $J_{\mu\nu}(\omega)$’s in Fig.4, reliable estimations are found possible.