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Alignment Echo of Spin-3/2 ^{9}Be Nuclei: Detection of Ultraslow Motion

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It is demonstrated that the alignment echo of ^{9}Be is quite useful for detecting ultraslow atomic motions in the metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$. The time scale of detectable atomic motion is between T_2 = 1.5 ms and T_1 of a few seconds. Similar to previous works of ^{2}H NMR, the Jeener–Broekaert sequence is used to create quadrupolar order for spin-$\frac{3}{2}$ nuclei upon nonselective excitations. Since the chemical and Knight shift distributions are not negligible for ^{9}Be, the proper choice of the dephasing time between the first and the second pulses is essential for achieving pure quadrupolar order. It is demonstrated experimentally that slow atomic motions contribute significantly to the decay of the alignment echo near the glass transition temperature.

Key Words: **alignment echo; quadrupolar order; ^{9}Be; ultraslow motion; metallic glass.**

INTRODUCTION

Recently, significant progress has been made in the development of metallic glasses. For instance, it was discovered that the metallic alloy $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Zr–Ti–Cu–Ni–Be) exhibits extraordinary glass formability as well as high resistance to crystallization in the supercooled liquid state (*1*). The study of slow atomic motion in metallic glasses is crucial for the understanding of the nature of glass transition as well as the thermal stability of metallic glasses. NMR has been used in the study of glass transition in polymers (*2*). It has distinct advantages in the study of atomic motion, such as the wide range of accessible time scale and the microscopic nature of the technique. In particular, various NMR techniques have been used to detect ultraslow atomic motion, including the techniques of dipolar order relaxation (*3*), ^{2}H alignment echo (*4*), the stimulated echo (*5, 6*), and two-dimensional chemical exchange (*2*). However, since the time scale of atomic motion near the glass transition temperature T_g is expected to be on the order of a second, NMR study of glass transition in metallic glasses is potentially hampered by the typical short spin–lattice relaxation time T_1 in metallic systems.

In this study we report the ideal features of ^{9}Be (spin-$\frac{3}{2}$) for studying slow atomic motions in metallic systems using the alignment echo technique. First, T_1 of ^{9}Be is very long, typically on the order of seconds (*7, 8*). Second, the quadrupole interaction is usually small enough (*7, 9, 10*) to allow nonselective excitations of both the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) and the satellite ($\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$) transitions by RF pulses. This permits the creation of quadrupolar order using the Jeener–Broekaert sequence (*4, 11*). Unlike ^{2}H, the Knight shift and the chemical shift distributions of ^{9}Be are not negligible. To achieve pure quadrupolar order, effects of such distributions need to be minimized. In the previous multiple-quantum filtration experiments in liquid-type environments, a 180° pulse is applied in the middle between the first and the second pulses to eliminate the effect of Zeeman interaction distribution (*12–14*). However, this method is limited by the inhomogeneity of the RF field throughout the sample (*15*); this is particularly true in metallic systems where the skin depth is very small. In this work, it is demonstrated that a proper time interval τ_1 between the first and the second pulses can be chosen conveniently for ^{9}Be to achieve pure quadrupolar order. The resulting alignment echo following the third pulse is shown to be sensitive to slow atomic motion activated near T_g.

BASIC THEORY

Assume that the truncated Hamiltonian in the rotating frame consists of the first-order quadrupole interaction and the Zeeman interaction given by

$$\mathcal{H} = \alpha(3I_z^2 - \hat{I}^2) + \beta I_z, \qquad [1]$$

where $\hat{I}^2 = I_x^2 + I_y^2 + I_z^2$, α is proportional to the nuclear quadrupole constant, and β is the frequency offset with respect to the RF frequency. Consider the evolution of the spin system under the Jeener–Broekaert sequence (*11*)

$$90^\circ_y\text{–}\tau_1\text{–}\theta'_{\phi'}\text{–}\tau_2\text{–}\theta''_{\phi''}\text{–}t \qquad [2]$$

with RF pulses being nonselective. In the current discussion, τ_2 is chosen to be larger than the dipole–dipole relaxation time T_2 and $\tau_1 < T_2$. θ' and θ'' are the flipping angles of the second and the third pulses, respectively; ϕ' and ϕ'' are the phases of the second and the third pulses, respectively, with respect to the first pulse. Without losing generality, we assume that the first pulse is a 90° pulse along the y-axis described by the Hamiltonian $\mathcal{H}_{rf} = (\pi/2)I_y$. Since the density operator in thermal equilibrium can be considered as $\rho(0) = I_z$, the first pulse

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TABLE 1
Irreducible Tensors T_{k0} Expressed in Terms of I_z

$$T_{00} = C_0^{(I)}$$

$$T_{10} = C_1^{(I)} I_z$$

$$T_{20} = \frac{1}{\sqrt{6}} C_2^{(I)}(3\hat{I}^2 - \hat{I}^2)$$

$$T_{30} = \frac{1}{\sqrt{10}} C_3^{(I)}[5I_z^3 - (3\hat{I}^2 - 1)I_z]$$

$$T_{40} = \frac{1}{2}\sqrt{\frac{35}{2}} C_4^{(I)}\left[I_z^4 - \frac{6\hat{I}^2 - 5}{7} I_z^2 + \frac{3(\hat{I}^4 - 2\hat{I}^2)}{35}\right]$$

$$T_{50} = \frac{3}{2}\sqrt{\frac{7}{2}} C_5^{(I)}\left[I_z^5 - \frac{5(2\hat{I}^2 - 3)}{9} I_z^3 + \frac{15\hat{I}^4 - 50\hat{I}^2 + 12}{63} I_z\right]$$

$$T_{60} = \frac{\sqrt{231}}{4} C_6^{(I)}\left[I_z^6 - \frac{15\hat{I}^2 - 35}{11} I_z^4 + \frac{5\hat{I}^4 - 25\hat{I}^2 + 14}{11} I_z^2 - \frac{5\hat{I}^6 - 40\hat{I}^4 + 60\hat{I}^2}{231}\right]$$

$$T_{70} = \frac{\sqrt{429}}{4} C_7^{(I)}\left[I_z^7 - \frac{21\hat{I}^2 - 70}{13} I_z^5 + \frac{7(15\hat{I}^4 - 105\hat{I}^2 + 101)}{143} I_z^3 - \frac{35\hat{I}^6 - 385\hat{I}^4 + 882\hat{I}^2 - 180}{429} I_z\right]$$

$$T_{80} = \frac{3}{8}\sqrt{\frac{715}{2}} C_8^{(I)}\left[I_z^8 - \frac{28\hat{I}^2 - 126}{15} I_z^6 + \frac{7(6\hat{I}^4 - 56\hat{I}^2 + 81)}{39} I_z^4 - \frac{2(210\hat{I}^6 - 3045\hat{I}^4 + 9898\hat{I}^2 - 4566)}{2145} I_z^2 + \frac{7(\hat{I}^8 - 20\hat{I}^6 + 108\hat{I}^4 - 144\hat{I}^2)}{1287}\right]$$

$$T_{90} = \frac{1}{8}\sqrt{\frac{12155}{2}} C_9^{(I)}\left[I_z^9 - \frac{36\hat{I}^2 - 210}{17} I_z^7 + \frac{21(6\hat{I}^4 - 72\hat{I}^2 + 145)}{85} I_z^5 - \frac{2(42\hat{I}^6 - 777\hat{I}^4 + 3402\hat{I}^2 - 2630)}{221} I_z^3 + \frac{3(105\hat{I}^8 - 2660\hat{I}^6 + 18844\hat{I}^4 - 36528\hat{I}^2 + 6720)}{12155} I_z\right]$$

$$C_k^{(I)} = \frac{1}{k!}\sqrt{\frac{2^k(2k+1)(2k)!(2I-k)!}{(2I+k+1)!}}$$

Note. The definition of the irreducible tensor operators is based on the convention adopted in Refs. (*17–19*) with the normalization condition $\mathrm{Tr}\{T_{kq}^{\dagger}T_{k'q'}\} = \delta_{kk'}\delta_{qq'}$.

simply converts the density operator to $\rho(0_+) = I_x$. The density operator immediately after the second pulse is given by

$$\rho(\tau_{1+}) = R(\theta'_{\phi'})\exp(-i\mathcal{H}\tau_1)I_x\exp(i\mathcal{H}\tau_1)R^{-1}(\theta'_{\phi'}), \quad [3]$$

where $R(\theta'_{\phi'}) = \exp(-i\phi' I_z)\exp(-i\theta' I_y)\exp(i\phi' I_z)$. Equation [3] can be written in the form

$$\rho(\tau_{1+}) = \exp(-i\phi' I_z)\{\cos\phi_{\mathrm{eff1}} A_x(\theta', \alpha'\tau_1) - \sin\phi_{\mathrm{eff1}} A_y(\theta', \alpha'\tau_1)\}\exp(i\phi' I_z), \quad [4a]$$

where

$$A_x(\theta, \alpha\tau) \equiv \exp(-i\theta I_y)\exp(-3i\alpha I_z^2\tau)I_x\exp(3i\alpha I_z^2\tau)\exp(i\theta I_y) \quad [4b]$$

and

$$A_y(\theta, \alpha\tau) \equiv \exp(-i\theta I_y)\exp(-3i\alpha I_z^2\tau)I_y\exp(3i\alpha I_z^2\tau)\exp(i\theta I_y) \quad [4c]$$

and $\phi_{\mathrm{eff1}} \equiv \phi' - \beta'\tau_1$. α' and β' are the values of α and β, respectively, during the time period τ_1. Since τ_2 is assumed to be longer than T_2, only the diagonal part of $\rho(\tau_{1+})$, ρ_{diag} (which commutes with I_z), persists at the end of the time interval τ_2. ρ_{diag} can be expressed as a linear combination of zeroth-order irreducible tensors T_{k0} (Table 1) with $k = 1, \ldots, 2I$. Since $A_x(\theta, \alpha\tau)$ changes sign upon 180° rotation around the y-axis, its diagonal part, $A_x^{\mathrm{diag}}(\theta, \alpha\tau)$, can only contain terms with odd ranks of T_{k0}. In contrast, since $A_y(\theta, \alpha\tau)$ remains identical upon 180° rotation around the y-axis, its diagonal part, $A_y^{\mathrm{diag}}(\theta, \alpha\tau)$, can only contain terms with even ranks of T_{k0}. Thus, ρ_{diag} can be expressed as

$$\rho_{\rm diag} = \cos\phi_{\rm eff1} A_x^{\rm diag}(\theta', \alpha'\tau_1) - \sin\phi_{\rm eff1} A_y^{\rm diag}(\theta', \alpha'\tau_1)$$
$$= \cos\phi_{\rm eff1} \sum_{{\rm odd}\,k} f_k(\theta', \alpha'\tau_1) T_{k0} - \sin\phi_{\rm eff1} \sum_{{\rm even}\,k} f_k(\theta', \alpha'\tau_1) T_{k0}, \quad [5]$$

where $k = 1, \ldots, 2I$ and $f_k(\theta', \alpha'\tau_1)$ are functions of θ' and τ_1. The main step in obtaining an explicit expression for Eq. [4] consists in working out the expression $G_{\pm}^{(I)}(\alpha) \equiv \exp(-i\alpha I_z^2) I_{\pm} \exp(i\alpha I_z^2)$ ($I_{\pm} = I_x \pm iI_y$), which can be carried out (although quite tedious for large I) using the exponential expansion method (*16*). An alternative method for deriving $G_{\pm}^{(I)}(\alpha)$, and thus the explicit expression of $f_k(\theta, \tau)$, is given in the Appendix. The first term of Eq. [5] originates from the Zeeman, octupolar orders, etc.; it contributes to both the satellite and central transitions upon the application of the third pulse. The second term of Eq. [5] originates from the quadrupolar, hexadecapolar orders, etc.; it can be verified easily that the $|\frac{1}{2}\rangle\langle-\frac{1}{2}|$ quantum coherence cannot be created by the third pulse from this term. Thus, the intensity of the central transition in the alignment echo is a direct measure of the presence of the Zeeman order.

The expression of the signal appearing after the third pulse is given by

$$S(t) = {\rm Tr}\{\exp(-3i\alpha'' I_z^2 t)\exp(-i\beta'' I_z t)\exp(-i\phi'' I_z)$$
$$\times \exp(-i\theta'' I_y)\exp(i\phi'' I_z)\rho_{\rm diag}\exp(-i\phi'' I_z)$$
$$\times \exp(i\theta'' I_y)\exp(i\phi'' I_z)\exp(\beta'' I_z t)\exp(3i\alpha'' I_z^2 t) I_+\}$$
$$= \exp(i\phi_{\rm eff2}){\rm Tr}\{\rho_{\rm diag}\exp(i\theta'' I_y)\exp(3i\alpha'' I_z^2 t) I_+$$
$$\times \exp(-3i\alpha'' I_z^2 t)\exp(-i\theta'' I_y)\}$$
$$= -\exp(i\phi_{\rm eff2}){\rm Tr}\{\rho_{\rm diag}\exp(-i\theta'' I_y)$$
$$\times \exp(3i\alpha'' I_z^2 t) I_+ \exp(-3i\alpha'' I_z^2 t)\exp(i\theta'' I_y)\}, \quad [6]$$

where $\phi_{\rm eff2} \equiv \phi'' + \beta'' t$, and α'' and β'' are the values of α and β, respectively, during the time interval t. Because of the possibility of atomic motions during the time period τ_2, α'' and β'' could be different from α' and β', respectively. Here, the correlation time of such atomic motion τ_c (the mean time the nucleus resides at a given environment) is assumed to be longer than T_2 and the jump process itself is considered to be sudden. In the last derivation of Eq. [6], $\exp(-i\pi I_z)\exp(\pm i\theta'' I_y)\exp(i\pi I_z) = \exp(\mp i\theta'' I_y)$ has been used. According to Eqs. [4b] and [4c], Eq. [6] can also be written as

$$S(t) = -\exp(i\phi_{\rm eff2}){\rm Tr}\{\rho_{\rm diag}[A_x(\theta'', -\alpha'' t)$$
$$+ iA_y(\theta'', -\alpha'' t)]\}. \quad [7]$$

Since $\rho_{\rm diag}$ commutes with I_z, only the diagonal parts of $A_x(\theta'', -\alpha'' t)$ and $A_y(\theta'', -\alpha'' t)$ contribute to the trace in Eq. [7]. Using the fact that ${\rm Tr}\{T_{k0}T_{k'0}\} = \delta_{kk'}$ (*17*) and Eq. [5], the signal $S(t)$ can be expressed in the simple form

$$S(t) = -\cos\phi_{\rm eff1}\exp(i\phi_{\rm eff2})$$
$$\times \sum_{{\rm odd}\,k} f_k(\theta', \alpha'\tau_1) f_k(\theta'', -\alpha'' t)$$
$$+ i\sin\phi_{\rm eff1}\exp(i\phi_{\rm eff2})$$
$$\times \sum_{{\rm even}\,k} f_k(\theta', \alpha'\tau_1) f_k(\theta'', -\alpha'' t). \quad [8]$$

In principle, the first term of Eq. [8] can be eliminated by setting $\phi_{\rm eff1} = \pm 90°$. However, this cannot be implemented by choosing the phase ϕ' if there is a significant β distribution $\delta\beta$. A straightforward method to eliminate this first term, and thus to eliminate the central transition, is to choose $\tau_1 \ll (\delta\beta)^{-1}$ and $\phi' = \pm 90°$. Under this condition, $\alpha\tau_1 \geq 1$ has to be satisfied to make the second term non-negligible, as can be seen from Eq. [4]. For a system with both $\delta\beta$ and α distribution $\delta\alpha$, such a choice of τ_1 can be made if $\delta\beta \ll \delta\alpha$, which is quite common for quadrupolar nuclei. This method of eliminating the central transition works also if the other interactions, represented by the Hamiltonian $\mathcal{H}'$, are present such as the second-order quadrupole interaction and the dipolar interactions; in this case, $(\delta\alpha)^{-1} \leq \tau_1 \ll (\delta|\mathcal{H}'|)^{-1}$ has to be satisfied.

For $I = \frac{3}{2}$, $f_k(\theta, \alpha\tau)$ is given by (see Appendix)

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{5}}\sin\theta[2 + 3\cos(6\alpha\tau)];$$
$$f_2(\theta, \alpha\tau) = \frac{3}{2}\sin(2\theta)\sin(6\alpha\tau);$$
$$f_3(\theta, \alpha\tau) = \frac{3}{2\sqrt{5}}\sin\theta[5\cos^2\theta - 1][1 - \cos(6\alpha\tau)]. \quad [9]$$

Therefore, the explicit expression of the signal can be obtained as

$$S(t) = -\frac{9}{4} i\sin(\phi' - \beta'\tau_1)e^{i(\phi'' + \beta'' t)}\sin(2\theta')$$
$$\times \sin(2\theta'')\sin(6\alpha'\tau_1)\sin(6\alpha'' t)$$
$$- \frac{1}{4}\cos(\phi' - \beta'\tau_1)e^{i(\phi'' + \beta'' t)}\sin\theta'\sin\theta''$$
$$\times \{(5 - 9\cos^2\theta' - 9\cos^2\theta''$$
$$+ 45\cos^2\theta'\cos^2\theta'') + (3 + 9\cos^2\theta'$$
$$+ 9\cos^2\theta'' - 45\cos^2\theta'\cos^2\theta'')$$
$$\times \cos(6\alpha'\tau_1) + (3 + 9\cos^2\theta'$$
$$+ 9\cos^2\theta'' - 45\cos^2\theta'\cos^2\theta'')$$
$$\times \cos(6\alpha'' t) + (9 - 9\cos^2\theta'$$
$$- 9\cos^2\theta'' + 45\cos^2\theta'\cos^2\theta'')$$
$$\times \cos(6\alpha'\tau_1)\cos(6\alpha'' t)\}. \quad [10]$$

Assuming no slow motion occurs during the time period τ_2, then $\alpha'' = \alpha'$ and $\beta'' = \beta'$ and Eq. [10] contains terms which form an echo at $t = \tau_1$. The signal of the echo can be derived easily from Eq. [10] and is given by

$$S_{\text{echo}}(t) = \frac{9}{8} C_{\text{even}} \sin(2\theta')\sin(2\theta'')\cos[6\alpha'(\tau_1 - t)] + \frac{1}{4} C_{\text{odd}} \sin\theta' \sin\theta'' \Big\{(5 - 9\cos^2\theta' - 9\cos^2\theta'' + 45\cos^2\theta'\cos^2\theta'') + \frac{1}{2}(9 - 9\cos^2\theta' - 9\cos^2\theta'' + 45\cos^2\theta'\cos^2\theta'')\cos[6\alpha'(\tau_1 - t)]\Big\}, \quad [11]$$

where $C_{\text{even}} = -\frac{1}{2}\{e^{i[\phi'+\phi''-\beta'(\tau_1-t)]} - e^{i[-\phi'+\phi''+\beta'(\tau_1+t)]}\}$ and $C_{\text{odd}} = -\frac{1}{2}\{e^{i[\phi'+\phi''-\beta'(\tau_1-t)]} + e^{i[-\phi'+\phi''+\beta'(\tau_1+t)]}\}$. At $\delta\beta\tau_1 \ll 1$, $C_{\text{even}} = -i\sin\phi' e^{i\phi''}$ and $C_{\text{odd}} = -\cos\phi' e^{i\phi''}$. Consider the case of $\phi' = 90°$ where $C_{\text{even}} = -ie^{i\phi''}$ and $C_{\text{odd}} = 0$; thus, the intensity of the echo associated with the central transition is zero. As τ_1 increases, C_{even} decreases in magnitude while C_{odd} increases in magnitude because of the effect of dephasing caused by the distribution of β (e.g., the powder pattern effect). In the limit of $\delta\beta\tau_1 \gg 1$, the effect of dephasing leads to $C_{\text{even}} = C_{\text{odd}} = -\frac{1}{2}e^{i[\phi'+\phi''-\beta'(\tau_1-t)]}$. For $\theta' = \theta'' = 45°$, the echo height associated with the satellite transition is 0.8125 at $\delta\beta\tau_1 \gg 1$ (normalized by the echo height at $\delta\beta\tau_1 \ll 1$); the echo height associated with the central transition is 0.4028 at $\delta\beta\tau_1 \gg 1$.

It is clear from Eq. [5] that pure Zeeman order cannot be created for $I = \frac{3}{2}$ nuclei by choosing $\beta'\tau_1 \ll 1$ and $\phi' = 0°$; both the Zeeman order and the octupolar order will be created under this condition. In contrast, pure quadrupolar order is created for ρ_{diag} under the condition of $\beta'\tau_1 \ll 1$ and $\phi' = 90°$. In this case, the signal $S_{\text{echo}}(t)$ is proportional to the single particle correlation function $\langle\sin(6\alpha(0)\tau_1)\sin(6\alpha(\tau_2)t)\rangle$ in the presence of slow atomic motion. The treatment of such a single particle correlation function as a result of motion has been discussed extensively (*4, 5*). In metallic glasses, the slow motion is due to random translational jumps of atoms. It is reasonable to assume that the electric field gradient at one nuclear site after a jump is independent of that before the jump. Furthermore, the number of possible electric field gradients at one nuclear site is large. With such a random atomic diffusion mechanism, the decay of the alignment echo can be simply described as

$$S_{\text{echo}}(t) \propto \exp(-\Omega\tau_2), \quad [12]$$

where Ω is the jump rate of atoms. Therefore, the time scale of the slow atomic motion can be directly obtained from the measurements of the decay rate of the quadrupole alignment echo. In addition to slow motion, the spin–lattice relaxation process also contributes to the decay of the spin alignment echo by destroying the quadrupolar order. The contribution of the spin–lattice relaxation process to pure quadrupolar order decay is much simpler than that to a mixture of Zeeman and octupolar orders and can be taken into account easily.

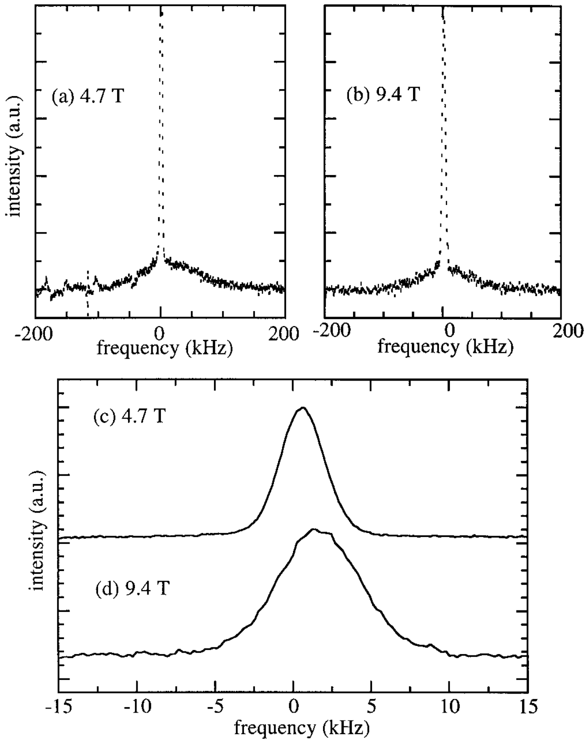

FIG. 1. (a) The satellite transition line of the ^{9}Be spectrum at 4.7 T and (b) 9.4 T. (c) The central transition peak of the ^{9}Be spectrum at 4.7 T and (d) 9.4 T.

EXPERIMENTAL

^{9}Be NMR is used to study the slow atomic motion in the metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ with the glass transition temperature $T_g = 596$ K (*1*). A home-built high temperature probe was used to conduct NMR experiments on a Chemagnetics CMX spectrometer at both 4.7 and 9.4 T. The 90° pulse employed is about 3 to 4 μs, which ensures the nonselective excitations of both the central and the satellite transitions.

Figure 1 shows the ^{9}Be spectra at 4.7 and 9.4 T at room temperature. The spectra were obtained by using the quadrupole echo pulse sequence. There is no obvious change of the spectra in the entire temperature range of current investigation. The spectra consist of two components. The full-width at half-height (FWHH) of the broad line is about (100 ± 10) kHz at both 4.7 and 9.4 T, as shown in Figs. 1a and 1b, respectively. Such field independence of the linewidth suggests that the broad line is associated with the satellite transitions broadened by the first-order quadrupolar interactions. The FWHH of the central peak is (3.6 ± 0.1) kHz at 4.7 T and (6.1 ± 0.2) kHz

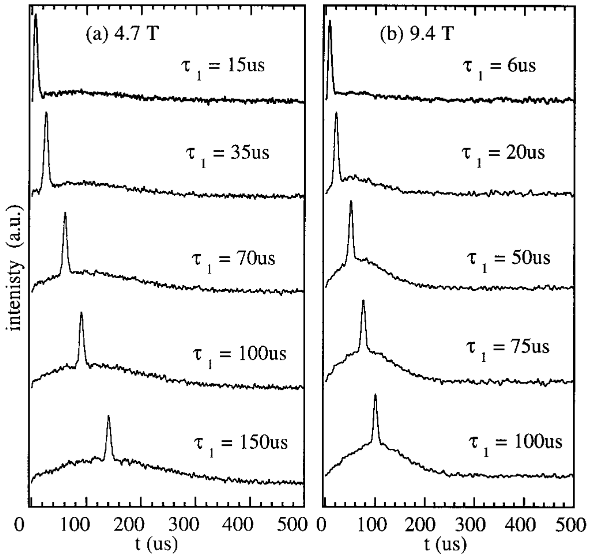

FIG. 2. (a) The ^{9}Be spin alignment echoes observed at 4.7 T with the dephasing time τ_1 at 15, 35, 70, 100, and 150 μs. (b) The spin alignment echoes observed at 9.4 T with the dephasing time τ_1 at 6, 20, 50, 75, and 100 μs.

at 9.4 T, as shown in Figs. 1c and 1d. The former is roughly half of the latter, suggesting that the broadening of the central peak is mainly due to the distribution of Zeeman interactions. The ^{9}Be spin–spin relaxation time (T_2), which is about 1.5 ms, is independent of the temperature within the entire investigated temperature range.

Figures 2a and 2b show the spin alignment echoes obtained by the Jeener–Broekaert sequence at 4.7 and 9.4 T, respectively. The slow-dephasing component of the echo corresponds to the central transition and the fast-dephasing component of the echo corresponds to the satellite transitions. As τ_1 increases, the intensity of the central transition increases while the intensity of the satellite transitions decreases, as shown in Fig. 2. This is in good agreement with Eq. [11]. The central transition is fully developed as τ_1 is increased to about 100 μs at 4.7 T and to about 50 μs at 9.4 T. To be quantitative, we use the measurements at 9.4 Tesla as an example. The echo height associated with the satellite transitions at $\tau_1 = 6$ μs is referred to as one. The total echo height at $\tau_1 = 100$ μs is 1.2. The echo height associated with the satellite transitions at $\tau_1 = 100$ μs is 0.7 and the echo height associated with the central transition at $\tau_1 = 100$ μs is 0.5. These values agree very well with the theoretical calculations given by Eq. [11]. Figure 2 shows that it is possible to create pure quadrupolar order using the condition of $(\delta\alpha)^{-1} \leq \tau_1 \ll (\delta\beta)^{-1}$.

The ^{9}Be spin–lattice relaxation time (T_1) is about 3 s at room temperature; it is inversely proportional to the observing temperature over the entire temperature range, as shown in Fig. 3a, where the saturation recovery of the nuclear magnetization M(τ) is plotted versus the recovery time τ for several measurement temperatures. This temperature dependence of T_1 agrees with the Korringa relaxation mechanism of electronic origin (*7, 8*). Figure 3b shows the spin alignment echo height versus τ_2 scaled by the observing temperature at 9.4 T and at 300, 425, 525, and 600 K. In these measurements, $\tau_1 = 15$ μs is used to ensure that only the pure quadrupolar order is created. Figure 3b shows that the decay rate of the spin alignment echo of quadrupolar order ($1/T_{QE}$) below 525 K is also proportional to the temperature. In contrast to $1/T_1$, the increase of $1/T_{QE}$ is much faster than a linear temperature dependence above 550 K, indicating the onset of slow atomic motion. This demonstrates that the created pure quadrupolar order provides a sensitive probe to the slow atomic motion near the glass transition temperature in the metallic glass.

CONCLUSIONS

We have presented a general method to calculate the spin alignment echo of quadrupolar nuclei under the Jeener–Broekaert sequence and in the presence of the distribution of both the first-order quadrupolar interactions and Zeeman interactions. The explicit formulas for $I = 1, \frac{3}{2}, \frac{5}{2}, 3, \frac{7}{2}$, and $\frac{9}{2}$ are given in the Appendix. The ^{9}Be NMR measurement in the investigated me-

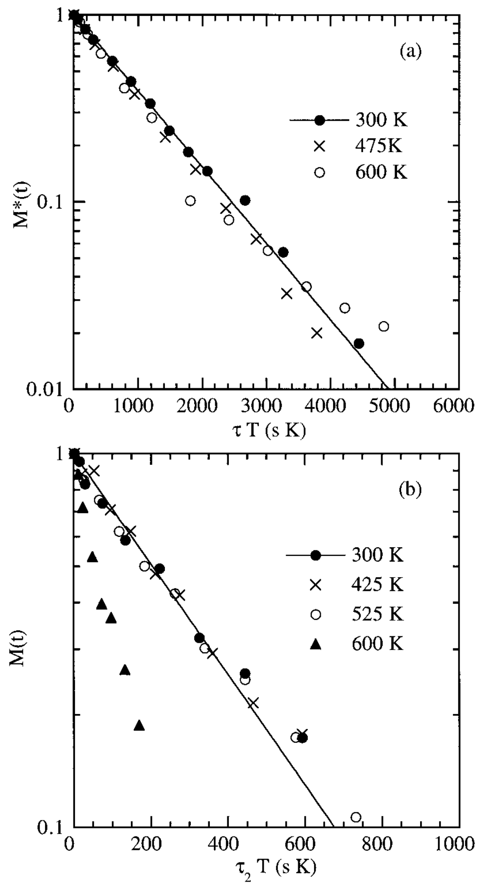

FIG. 3. (a) The saturation recovery curves (at 9.4 T) of magnetization $M^*(\tau)$ versus the recovery time τ, which is scaled by the observation temperature at 300, 475, and 600 K, and $M^*(\tau)$ is defined as $M^*(\tau) = [M(\infty) - M(\tau)]/[M(\infty) - M(0)]$. (b) The normalized height of the spin alignment echoes versus the decay time τ_2, which is scaled by the observing temperature at 300, 425, 525, and 600 K and at 9.4 T.

tallic glass sample is in good agreement with the theoretical calculations for $I = \frac{3}{2}$. It is demonstrated that the pure quadrupolar order can be created by choosing the dephasing time τ_1 such that the dephasing caused by the first-order quadrupolar interactions is fully developed, while the dephasing caused by the Zeeman interactions is negligible. The created quadrupolar order for ^{9}Be nuclei is proved to be a sensitive probe for slow atomic motions in the investigated metallic glass system.

APPENDIX

A general method for deriving $f_k(\theta, \alpha\tau)$ defined in Eq. [5] is described in this Appendix. As mentioned earlier, the key to solving this problem is to solve $G_{\pm}^{(I)}(\gamma) \equiv \exp(-i\gamma I_z^2)I_{\pm}\exp(i\gamma I_z^2)$ for nuclei with spin quantum number I.

The identity

$$\exp(-i\gamma I_z^2)I_{\pm} = I_{\pm}\exp[-i\gamma(I_z \pm 1)^2], \qquad [A1]$$

which can be verified easily, provides a clue for solving $G_{\pm}^{(I)}(\gamma)$ with an arbitrary I. From Eq. [A1] it follows that $G_{\pm}^{(I)}(\gamma) = I_{\pm}\exp[-i\gamma(1 \pm 2I_z)]$. This shows that the problem can be formulated in the form of a linear differential equation. This can be seen clearly from the identity

$$(I_z \pm I)[I_z \pm (I-1)]\cdots[I_z \pm (-I+2)][I_z \pm (-I+1)] \times [I_z \pm (-I)] = 0, \qquad [A2]$$

which is identical to

$$I_{\pm}(I_z \pm I)[I_z \pm (I-1)]\cdots[I_z \pm (-I+2)] [I_z \pm (-I+1)] = 0. \qquad [A3]$$

Since

$$\frac{\partial^n}{\partial\gamma^n} G_{\pm}^{(I)}(\gamma) = (-i)^n I_{\pm}(1 \pm 2I_z)^n \times exp[-i\gamma(1 \pm 2I_z)], \qquad [A4]$$

Eqs. [A3] and [A4] show that the differential equation of operators

$$\left[\frac{\partial}{\partial\gamma} - i(2I-1)\right]\left[\frac{\partial}{\partial\gamma} - i(2I-3)\right]\cdots \left[\frac{\partial}{\partial\gamma} + i(2I-1)\right]G_{\pm}^{(I)}(\gamma) = 0 \qquad [A5]$$

is valid. The eigenvalues of the characteristic equation for this linear differential equation are

$$-(2I-1)i,\ -(2I-3)i,\ \ldots,\ (2I-3)i,\ (2I-1)i. \qquad [A6]$$

Therefore, the solution of $G_{\pm}^{(I)}(\gamma)$ can be expressed as

$$G_{\pm}^{(I)}(\gamma) = I_{\pm}\sum_{n=0}^{(2I-1)/2} A_{2n}\cos(2n\gamma) + I_{\pm}\sum_{n=1}^{(2I-1)/2} B_{2n}\sin(2n\gamma) \qquad [A7]$$

for a half-integer I and as

$$G_{\pm}^{(I)}(\gamma) = I_{\pm}\sum_{n=0}^{I-1}\{C_{2n+1}\cos[(2n+1)\gamma] + D_{2n+1}\sin[(2n+1)\gamma]\} \qquad [A8]$$

for an integer I. The coefficients A_{2n}, B_{2n}, C_{2n+1}, andD_{2n+1}, which are operators independent of γ, can be determined by the initial conditions $(\partial^n/\partial\gamma^n)G_{\pm}^{(I)}(0) = (-i)^n I_{\pm}(1 \pm 2I_z)^n$. The final solution of Eq. [A5] for a half-integer I is

$$G_{\pm}^{(I)}(\gamma) = [1\ \cos 2\gamma\ \cos 4\gamma \cdots \cos(2I-1)\gamma] \times \begin{bmatrix} 1 & 1 & 1 & \cdots & 1 \\ 0 & 2^2 & 4^2 & \cdots & (2I-1)^2 \\ 0 & 2^4 & 4^4 & \cdots & (2I-1)^4 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 2^{2I-1} & 4^{2I-1} & \cdots & (2I-1)^{2I-1} \end{bmatrix}^{-1} \times \begin{bmatrix} I_{\pm} \\ I_{\pm}(1 \pm 2I_z)^2 \\ I_{\pm}(1 \pm 2I_z)^4 \\ \vdots \\ I_{\pm}(1 \pm 2I_z)^{2I-1} \end{bmatrix} - i[\sin 2\gamma\ \sin 4\gamma \cdots \sin(2I-1)\gamma] \times \begin{bmatrix} 2 & 4 & \cdots & (2I-1) \\ 2^3 & 4^3 & \cdots & (2I-1)^3 \\ \vdots & \vdots & \vdots & \vdots \\ 2^{2I-2} & 4^{2I-2} & \cdots & (2I-1)^{2I-2} \end{bmatrix}^{-1} \times \begin{bmatrix} I_{\pm}(1 \pm I_z) \\ I_{\pm}(1 \pm I_z)^3 \\ \vdots \\ I_{\pm}(1 \pm I_z)^{2I-2} \end{bmatrix} \qquad [A9]$$

and the final solution of Eq. [A5] for an integer I is

$$G_{\pm}^{(I)}(\gamma) = [\cos\gamma\ \cos 3\gamma\ \cos 5\gamma \cdots \cos(2I-1)\gamma] \times \begin{bmatrix} 1 & 1 & 1 & \cdots & 1 \\ 1 & 3^2 & 5^2 & \cdots & (2I-1)^2 \\ 1 & 3^4 & 5^4 & \cdots & (2I-1)^4 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & 3^{2I-2} & 3^{2I-2} & \cdots & (2I-1)^{2I-2} \end{bmatrix}^{-1}$$

TABLE 2
Irreducible Tensors $T_{k\pm1}$ Expressed in Terms of I_+, I_-, and I_z

k	$T_{k\pm1}$
1	$\mp\frac{1}{\sqrt{2}}C_1^{(I)}I_\pm$
2	$\mp\frac{1}{2}C_2^{(I)}[I_zI_\pm + I_\pm I_z]$
3	$\mp\frac{1}{4}\sqrt{\frac{3}{10}}C_3^{(I)}\left[\left(5I_z^2 - \hat{I}^2 - \frac{1}{2}\right)I_\pm + I_\pm\left(5I_z^2 - \hat{I}^2 - \frac{1}{2}\right)\right]$
4	$\mp\frac{\sqrt{14}}{4}C_4^{(I)}\left\{\left[I_z^3 - \frac{3\hat{I}^2+1}{7}I_z\right]I_\pm + I_\pm\left[I_z^3 - \frac{3\hat{I}^2+1}{7}I_z\right]\right\}$
5	$\mp\frac{\sqrt{105}}{8}C_5^{(I)}\left\{\left[I_z^4 - \frac{2\hat{I}^2}{3}I_z^2 + \frac{2\hat{I}^4 - 2\hat{I}^2 + 3}{42}\right]I_\pm + I_\pm\left[I_z^4 - \frac{2\hat{I}^2}{3}I_z^2 + \frac{2\hat{I}^4 - 2\hat{I}^2 + 3}{42}\right]\right\}$
6	$\mp\frac{3\sqrt{22}}{8}C_6^{(I)}\left\{\left[I_z^5 - \frac{10\hat{I}^2 - 5}{11}I_z^3 + \frac{5\hat{I}^4 - 10\hat{I}^2 + 12}{33}I_z\right]I_\pm + I_\pm\left[I_z^5 - \frac{10\hat{I}^2 - 5}{11}I_z^3 + \frac{5\hat{I}^4 - 10\hat{I}^2 + 12}{33}I_z\right]\right\}$
7	$\mp\frac{\sqrt{6006}}{32}C_7^{(I)}\left\{\left[I_z^6 - \frac{30\hat{I}^2 - 35}{26}I_z^4 + \frac{45\hat{I}^4 - 150\hat{I}^2 + 182}{143}I_z^2 - \frac{5(4\hat{I}^6 - 26\hat{I}^4 + 54\hat{I}^2 + 45)}{858}\right]I_\pm\right.$
	$\left.+I_\pm\left[I_z^6 - \frac{30\hat{I}^2 - 35}{26}I_z^4 + \frac{45\hat{I}^4 - 150\hat{I}^2 + 182}{143}I_z^2 - \frac{5(4\hat{I}^6 - 26\hat{I}^4 + 54\hat{I}^2 + 45}{858}\right]\right\}$
8	$\mp\frac{\sqrt{715}}{8}C_8^{(I)}\left\{\left[I_z^7 - \frac{7\hat{I}^2 - 14}{5}I_z^5 + \frac{7\hat{I}^4 - 35\hat{I}^2 + 49}{13}I_z^3 - \frac{35\hat{I}^6 - 315\hat{I}^4 + 854\hat{I}^2 + 372}{715}I_z\right]I_\pm\right.$
	$\left.+ I_\pm\left[I_z^7 - \frac{7\hat{I}^2 - 14}{5}I_z^5 + \frac{7\hat{I}^4 - 35\hat{I}^2 + 49}{13}I_z^3 - \frac{35\hat{I}^6 - 315\hat{I}^4 + 854\hat{I}^2 + 372}{715}I_z\right]\right\}$
9	$\mp\frac{3\sqrt{2431}}{32}C_9^{(I)}\left\{\left[I_z^8 - \frac{28\hat{I}^2 - 84}{17}I_z^6 + \frac{2(7\hat{I}^4 - 49\hat{I}^2 + 84)}{17}I_z^4 - \frac{7\hat{I}^6 - 336\hat{I}^4 + 1176\hat{I}^2 + 32}{221}I_z^2 + \frac{14\hat{I}^8 - 252\hat{I}^6 + 1414\hat{I}^4 - 1302\hat{I}^2 + 2205}{4862}\right]I_\pm\right.$
	$\left.+ I_\pm\left[I_z^8 - \frac{28\hat{I}^2 - 84}{17}I_z^6 + \frac{2(7\hat{I}^4 - 49\hat{I}^2 + 84)}{17}I_z^4 - \frac{7\hat{I}^6 - 336\hat{I}^4 + 1176\hat{I}^2 + 32}{221}I_z^2 + \frac{14\hat{I}^8 - 252\hat{I}^6 + 1414\hat{I}^4 - 1302\hat{I}^2 + 2205}{4862}\right]\right\}$

$$\times\begin{bmatrix} I_\pm \\ I_\pm(1 \pm 2I_z)^2 \\ I_\pm(1 \pm 2I_z)^4 \\ \vdots \\ I_\pm(1 \pm 2I_z)^{2I-2} \end{bmatrix}$$

$$- i[\sin\gamma \ \sin 3\gamma \ \sin 5\gamma \cdots \sin(2I-1)\gamma]$$

$$\times\begin{bmatrix} 1 & 3 & 5 & \cdots & 2I-1 \\ 1 & 3^3 & 5^3 & \cdots & (2I-1)^3 \\ 1 & 3^5 & 5^5 & \cdots & (2I-1)^5 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & 3^{2I-1} & 5^{2I-1} & \cdots & (2I-1)^{2I-1} \end{bmatrix}^{-1}$$

$$\times\begin{bmatrix} I_\pm(1 \pm 2I_z) \\ I_\pm(1 \pm 2I_z)^3 \\ I_\pm(1 \pm 2I_z)^5 \\ \vdots \\ I_\pm(1 \pm 2I_z)^{2I-1} \end{bmatrix}. \quad \text{[A10]}$$

It is straightforward to obtain the explicit expressions of $G_\pm^{(I)}(\gamma)$ with Eqs. [A9] and [A10]. Using Table 3, $I_\pm(1 \pm 2I_z)^n$ can be expressed in terms of the spherical irreducible tensors $T_{k\pm1}$ given in Table 2. Thus, the explicit expressions of $G_\pm^{(I)}(\gamma)$ in terms of the spherical irreducible tensors can be obtained for $I = 1, \frac{3}{2}, \frac{5}{2}, 3, \frac{7}{2}, \frac{9}{2}$ as below:

$$G_\pm^{(1)}(3\alpha\tau) = \mp 2\cos(3\alpha\tau)T_{1\pm1} + 2i\sin(3\alpha\tau)T_{2\pm1} \quad \text{[A11]}$$

$$G_\pm^{(3/2)}(3\alpha\tau) = \mp\left\{\sqrt{\frac{2}{5}}[2 + 3\cos(6\alpha\tau)]T_{1\pm1} + 2\sqrt{\frac{3}{5}}[-1 + \cos(6\alpha\tau)]T_{3\pm1}\right\} + i\sqrt{6}\sin(6\alpha\tau)T_{2\pm1} \quad \text{[A12]}$$

$$G_\pm^{(5/2)}(3\alpha\tau) = \mp\left\{\frac{1}{\sqrt{35}}[9 + 16\cos(6\alpha\tau) + 10\cos(12\alpha\tau)]T_{1\pm1} + \frac{1}{\sqrt{15}}[-6 - 4\cos(6\alpha\tau) + 10\cos(12\alpha\tau)]T_{3\pm1} + \sqrt{\frac{10}{21}}[3 - 4\cos(6\alpha\tau) + \cos(12\alpha\tau)]T_{5\pm1}\right\}$$

TABLE 3
$(-1)^n I_\pm(1 \pm 2I_z)^n$ Expressed in Terms of Irreducible Tensors $T_{k\pm1}$

n	$(-1)^n I_\pm(1 \pm 2I_z)^n$
1	$\frac{\sqrt{6}}{3C_2^{(I)}} T_{2\pm1}$
2	$\mp\left\{\frac{8\sqrt{3}}{15C_3^{(I)}} T_{3\pm1} - \frac{\sqrt{2}}{5C_1^{(I)}}(3 - 4\hat{I}^2)T_{1\pm1}\right\}$
3	$\frac{4\sqrt{5}}{C_4^{(I)}} T_{4\pm1} - \frac{\sqrt{6}}{21C_2^{(I)}}(17 - 12\hat{I}^2)T_{2\pm1}$
4	$\mp\left\{\frac{16\sqrt{30}}{5C_5^{(I)}} T_{5\pm1} - \frac{16\sqrt{3}}{45C_3^{(I)}}(9 - 4\hat{I}^2)T_{3\pm1} + \frac{\sqrt{2}}{35C_1^{(I)}}(51 - 104\hat{I}^2 + 48\hat{I}^4)T_{1\pm1}\right\}$
5	$\frac{16\sqrt{42}}{3C_6^{(I)}} T_{6\pm1} - \frac{\sqrt{5}}{11C_4^{(I)}}(520 - 160\hat{I}^2)T_{4\pm1} + \frac{\sqrt{6}}{63C_2^{(I)}}(261 - 280\hat{I}^2 + 80\hat{I}^4)T_{2\pm1}$
6	$\mp\left\{\frac{128\sqrt{14}}{7C_7^{(I)}} T_{7\pm1} - \frac{\sqrt{30}}{13C_5^{(I)}}(848 - 192\hat{I}^2)T_{5\pm1} + \frac{2\sqrt{3}}{495C_3^{(I)}}(7212 - 4960\hat{I}^2 + 960\hat{I}^4) - \frac{\sqrt{2}}{105C_1^{(I)}}(783 - 1884\hat{I}^2 + 1360\hat{I}^4 - 320\hat{I}^6)T_{1\pm1}\right\}T_{3\pm1}$
7	$\frac{96\sqrt{2}}{C_8^{(I)}} T_{8\pm1} - \frac{\sqrt{42}}{15C_6^{(I)}}(2576 - 448\hat{I}^2)T_{6\pm1} + \frac{\sqrt{5}}{143C_4^{(I)}}(99092 - 48160\hat{I}^2 + 6720\hat{I}^4)T_{4\pm1} - \frac{\sqrt{6}}{99C_2^{(I)}}(3543 - 4508\hat{I}^2 + 2000\hat{I}^4 - 320\hat{I}^6)T_{2\pm1}$
8	$\mp\left\{\frac{256\sqrt{10}}{3C_9^{(I)}} T_{9\pm1} - \frac{\sqrt{14}}{17C_7^{(I)}}(14848 - 2048\hat{I}^2)T_{7\pm1} + \frac{\sqrt{30}}{65C_5^{(I)}}(93408 - 34048\hat{I}^2 + 3584\hat{I}^4)T_{5\pm1} - \frac{\sqrt{3}}{6435C_3^{(I)}}(2491872 - 2067072\hat{I}^2 + 627200\hat{I}^4 - 71680\hat{I}^6)T_{3\pm1} + \frac{\sqrt{2}}{165C_1^{(I)}}(10629 - 27696\hat{I}^2 + 24032\hat{I}^4 - 8960\hat{I}^6 + 1280\hat{I}^8)T_{1\pm1}\right\}$

$$+ i\left\{\sqrt{\frac{2}{7}}[4\sin(6\alpha\tau) + 5\sin(12\alpha\tau)]T_{2\pm1} - 2\sqrt{\frac{5}{7}}[2\sin(6\alpha\tau) - \sin(12\alpha\tau)]T_{4\pm1}\right\} \quad \text{[A13]}$$

$$G_\pm^{(3)}(3\alpha\tau) = \mp\left\{\sqrt{\frac{2}{7}}[6\cos(3\alpha\tau) + 5\cos(9\alpha\tau) + 3\cos(15\alpha\tau)]T_{1\pm1} - \frac{1}{\sqrt{2}}[30\cos(3\alpha\tau) - 39\cos(9\alpha\tau) + 9\cos(15\alpha\tau)]T_{3\pm1} + \sqrt{\frac{10}{7}}[2\cos(3\alpha\tau) - 3\cos(9\alpha\tau) + \cos(15\alpha\tau)]T_{5\pm1}\right\}$$
$$+ i\left\{\frac{1}{80\sqrt{14}}[320\sin(3\alpha\tau) - 75\sin(9\alpha\tau) + 926\sin(12\alpha\tau)]T_{2\pm1} - \sqrt{\frac{10}{77}}[6\sin(3\alpha\tau) + 8\sin(9\alpha\tau) - 6\sin(12\alpha\tau)]T_{4\pm1} + \sqrt{\frac{2}{11}}[10\sin(3\alpha\tau) - 5\sin(9\alpha\tau) + \sin(12\alpha\tau)]T_{6\pm1}\right\} \quad \text{[A14]}$$

$$G_\pm^{(7/2)}(3\alpha\tau) = \mp\left\{\frac{1}{\sqrt{21}}[8 + 15\cos(6\alpha\tau) + 12\cos(12\alpha\tau) + 7\cos(18\alpha\tau)]T_{1\pm1} - \sqrt{\frac{2}{11}}[4 + 5\cos(6\alpha\tau) - 2\cos(12\alpha\tau) - 7\cos(18\alpha\tau)]T_{3\pm1} + \frac{1}{13}\sqrt{\frac{113}{14}}[40 + 5\cos(6\alpha\tau) - 80\cos(12\alpha\tau) + 35\cos(18\alpha\tau)]T_{5\pm1} - \sqrt{\frac{7}{429}}[20 - 30\cos(6\alpha\tau) + 12\cos(12\alpha\tau) - 2\cos(18\alpha\tau)]T_{7\pm1}\right\}$$
$$+ i\left\{\frac{1}{\sqrt{7}}[5\sin(6\alpha\tau) + 8\sin(12\alpha\tau) + 7\sin(18\alpha\tau)]T_{2\pm1} - \sqrt{\frac{10}{77}}[9\sin(6\alpha\tau) + 6\sin(12\alpha\tau) - 7\sin(18\alpha\tau)]T_{4\pm1}\right.$$

TABLE 4
Reduced Wigner Rotation Elements $d^{(k)}_{0\pm 1}(\theta)$

k	$d^{(k)}_{0\pm 1}(\theta)$
1	$\pm \frac{1}{\sqrt{2}} \sin\theta$
2	$\pm \sqrt{\frac{3}{8}} \sin 2\theta$
3	$\pm \frac{\sqrt{3}}{4} \sin\theta(5\cos^2\theta - 1)$
4	$\pm \frac{\sqrt{5}}{16} \sin 2\theta(1 + 7\cos 2\theta)$
5	$\pm \frac{\sqrt{30}}{128} \sin\theta(15 + 28\cos 2\theta + 21\cos 4\theta)$
6	$\pm \frac{\sqrt{42}}{256} \sin 2\theta(19 + 12\cos 2\theta + 33\cos 4\theta)$
7	$\pm \frac{\sqrt{14}}{2048} \sin\theta(350 + 675\cos 2\theta + 594\cos 4\theta + 429\cos 6\theta)$
8	$\pm \frac{3\sqrt{2}}{4096} \sin 2\theta(178 + 869\cos 2\theta + 286\cos 4\theta + 715\cos 6\theta)$
9	$\pm \frac{3\sqrt{10}}{32768} \sin\theta(2205 + 4312\cos 2\theta + 4004\cos 4\theta + 3432\cos 6\theta + 2431\cos 8\theta)$

Note. The reduced Wigner rotation elements of $k = 1, 2, 3$ are given in Ref. (*17*). The other elements of $k = 4, 5, 6, 7, 8, 9$ are obtained by using the formula given in Ref. (*19*).

$$+ \sqrt{\frac{7}{11}}[5\sin(6\alpha\tau) - 4\sin(12\alpha\tau) + \sin(18\alpha\tau)]T_{6\pm 1}\Big\} \quad [A15]$$

$$\begin{aligned} G^{(9/2)}_{\pm}(3\alpha\tau) = \mp\Big\{ & \frac{1}{\sqrt{165}}[25 + 48\cos(6\alpha\tau) + 42\cos(12\alpha\tau) + 32\cos(18\alpha\tau) + 18\cos(24\alpha\tau)]T_{1\pm 1} \\ & - \frac{1}{\sqrt{715}}[50 + 76\cos(6\alpha\tau) + 14\cos(12\alpha\tau) - 56\cos(18\alpha\tau) - 84\cos(24\alpha\tau)]T_{3\pm 1} \\ & + \sqrt{\frac{2}{13}}[5 + 4\cos(6\alpha\tau) - 7\cos(12\alpha\tau) - 8\cos(18\alpha\tau) + 6\cos(24\alpha\tau)]T_{5\pm 1} \\ & - \sqrt{\frac{14}{7293}}[50 - 12\cos(6\alpha\tau) - 96\cos(12\alpha\tau) + 76\cos(18\alpha\tau) - 18\cos(24\alpha\tau)]T_{7\pm 1} + \sqrt{\frac{2}{2431}} \\ & \times [105 - 168\cos(6\alpha\tau) + 84\cos(12\alpha\tau) - 24\cos(18\alpha\tau) + 3\cos(24\alpha\tau)]T_{9\pm 1}\Big\} \\ & + i\Big\{\sqrt{\frac{2}{11}}[4\sin(6\alpha\tau) + 7\sin(12\alpha\tau) + 8\sin(18\alpha\tau) + 6\sin(24\alpha\tau)]T_{2\pm 1} \\ & - \frac{1}{\sqrt{143}}[36\sin(6\alpha\tau) + 42\sin(12\alpha\tau) + 8\sin(18\alpha\tau) - 36\sin(24\alpha\tau)]T_{4\pm 1} \\ & + \sqrt{\frac{14}{55}}[8\sin(6\alpha\tau) + 2\sin(12\alpha\tau) - 8\sin(18\alpha\tau) + 3\sin(24\alpha\tau)]T_{6\pm 1} \\ & - \sqrt{\frac{2}{175}}[84\sin(6\alpha\tau) - 84\sin(12\alpha\tau) + 36\sin(18\alpha\tau) - \sin(24\alpha\tau)]T_{8\pm 1}\Big\}. \end{aligned} \quad [A16]$$

Under the rotation $R = \exp(-i\theta I_y)$, $T_{k\pm 1}$ is converted into $\Sigma^{k}_{q=-k} d^{(k)}_{q\pm 1}(\theta)T_{kq}$, where $d^{(k)}_{q\pm 1}(\theta)$ are the reduced Wigner rotation matrix elements listed in Table 4 for $q = 0$ and $k = 1, 2, \ldots, 9$. The diagonal part of $RT_{k\pm 1}R^{-1}$ is $d^{(k)}_{0\pm 1}(\theta)T_{k0}$. According to the definition of the function $f_k(\theta, \alpha\tau)$ (Eq. [5]), the diagonal part of $\frac{1}{2}R\{G^{(I)}_{+} + G^{(I)}_{-}\}R^{-1}$ is $\Sigma_{\text{odd } k} f_k(\theta, \alpha\tau)\, T_{k0}$ and the diagonal part of $1/2i\ R\{G^{(I)}_{+} - G^{(I)}_{-}\}R^{-1}$ is $\Sigma_{\text{even } k}\ f_k(\theta,$

$\alpha\tau)T_{k0}$. Therefore, using Table 4 and Eqs. [A11]–[A16], it is straightforward to obtain $f_k(\theta, \alpha\tau)$ as follows:

For spin $I = 1$,

$$f_1(\theta, \alpha\tau) = -\sqrt{2}\cos 3\alpha\tau \sin\theta,$$
$$f_2(\theta, \alpha\tau) = \sqrt{\frac{3}{2}}\sin 3\alpha\tau \sin 2\theta. \qquad [A17]$$

For spin $I = \frac{3}{2}$,

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{5}}[2 + 3\cos(6\alpha\tau)]\sin\theta,$$
$$f_2(\theta, \alpha\tau) = \frac{3}{2}\sin(6\alpha\tau)\sin 2\theta$$
$$f_3(\theta, \alpha\tau) = -\frac{3}{2\sqrt{5}}[-1 + \cos(6\alpha\tau)] \times \sin\theta(5\cos^2\theta - 1). \qquad [A18]$$

For spin $I = \frac{5}{2}$,

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{70}}[9 + 16\cos(6\alpha\tau) + 10\cos(12\alpha\tau)]\sin\theta$$
$$f_2(\theta, \alpha\tau) = \frac{1}{2}\sqrt{\frac{3}{7}}[4\sin(6\alpha\tau) + 5\sin(12\alpha\tau)]\sin 2\theta$$
$$f_3(\theta, \alpha\tau) = -\frac{1}{2\sqrt{5}}[-3 - 2\cos(6\alpha\tau) + 5\cos(12\alpha\tau)]\sin\theta(5\cos^2\theta - 1)$$
$$f_4(\theta, \alpha\tau) = \frac{5}{8\sqrt{7}}[-2\sin(6\alpha\tau) + \sin(12\alpha\tau)] \times \sin 2\theta(1 + 7\cos 2\theta)$$
$$f_5(\theta, \alpha\tau) = -\frac{5}{64\sqrt{7}}[3 - 4\cos(6\alpha\tau) + \cos(12\alpha\tau)] \times \sin\theta[15 + 28\cos 2\theta + 21\cos 4\theta]. \qquad [A19]$$

For spin $I = 3$,

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{7}}[6\cos(3\alpha\tau) + 5\cos(9\alpha\tau) + 3\cos(15\alpha\tau)]\sin\theta$$
$$f_2(\theta, \alpha\tau) = \frac{1}{320}\sqrt{\frac{3}{7}}[320\sin(3\alpha\tau) - 75\sin(9\alpha\tau) + 926\sin(15\alpha\tau)]\sin 2\theta$$
$$f_3(\theta, \alpha\tau) = \frac{\sqrt{6}}{8}[30\cos(3\alpha\tau) - 39\cos(9\alpha\tau) + 9\cos(15\alpha\tau)]\sin\theta(5\cos^2\theta - 1)$$
$$f_4(\theta, \alpha\tau) = -\frac{5}{4\sqrt{154}}[3\sin(3\alpha\tau) + 4\sin(9\alpha\tau) - 3\sin(15\alpha\tau)]\sin 2\theta(1 + 7\cos 2\theta)$$
$$f_5(\theta, \alpha\tau) = -\frac{5}{64}\sqrt{\frac{3}{7}}[2\cos(3\alpha\tau) - 3\cos(9\alpha\tau) + \cos(15\alpha\tau)] \times \sin\theta[15 + 28\cos 2\theta + 21\cos 4\theta]$$
$$f_6(\theta, \alpha\tau) = \frac{1}{128}\sqrt{\frac{21}{11}}[10\sin(3\alpha\tau) - 5\sin(9\alpha\tau) + \sin(15\alpha\tau)] \times \sin 2\theta(19 + 12\cos 2\theta + 33\cos 4\theta). \qquad [A20]$$

For spin $I = \frac{7}{2}$,

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{42}}[8 + 15\cos(6\alpha\tau) + 12\cos(12\alpha\tau) + 7\cos(18\alpha\tau)]\sin\theta$$
$$f_2(\theta, \alpha\tau) = \sqrt{\frac{3}{56}}[5\sin(6\alpha\tau) + 8\sin(12\alpha\tau) + 7\sin(18\alpha\tau)]\sin 2\theta$$
$$f_3(\theta, \alpha\tau) = \frac{1}{2}\sqrt{\frac{3}{22}}[4 + 5\cos(6\alpha\tau) - 2\cos(12\alpha\tau) - 7\cos(18\alpha\tau)]\sin\theta(5\cos^2\theta - 1)$$
$$f_4(\theta, \alpha\tau) = -\frac{5}{8\sqrt{154}}[9\sin(6\alpha\tau) + 6\sin(12\alpha\tau) - 7\sin(18\alpha\tau)]\sin 2\theta(1 + 7\cos 2\theta)$$
$$f_5(\theta, \alpha\tau) = -\frac{1}{1664}\sqrt{\frac{78}{7}}[40 + 5\cos(6\alpha\tau) - 80\cos(12\alpha\tau) + 35\cos(18\alpha\tau)] \times \sin\theta[15 + 28\cos 2\theta + 21\cos 4\theta]$$
$$f_6(\theta, \alpha\tau) = \frac{7}{256}\sqrt{\frac{6}{11}}[5\sin(6\alpha\tau) - 4\sin(12\alpha\tau) + \sin(18\alpha\tau)] \times \sin 2\theta(19 + 12\cos 2\theta + 33\cos 4\theta)$$
$$f_7(\theta, \alpha\tau) = \frac{7}{512\sqrt{858}}[10 - 15\cos(6\alpha\tau)$$

$$+ 6\cos(12\alpha\tau) - \cos(18\alpha\tau)] \times \sin\theta(350 + 675\cos 2\theta + 594\cos 4\theta + 429\cos 6\theta). \quad [A21]$$

For spin $I = \frac{9}{2}$,

$$f_1(\theta, \alpha\tau) = -\frac{1}{\sqrt{330}}[25 + 48\cos(6\alpha\tau) + 42\cos(12\alpha\tau) + 32\cos(18\alpha\tau) + 18\cos(24\alpha\tau)]\sin\theta$$

$$f_2(\theta, \alpha\tau) = \frac{1}{2}\sqrt{\frac{3}{11}}[4\sin(6\alpha\tau) + 7\sin(12\alpha\tau) + 8\sin(18\alpha\tau) + 6\sin(24\alpha\tau)]\sin 2\theta$$

$$f_3(\theta, \alpha\tau) = \frac{1}{2}\sqrt{\frac{3}{715}}[25 + 38\cos(6\alpha\tau) + 7\cos(12\alpha\tau) - 28\cos(18\alpha\tau) - 42\cos(24\alpha\tau)]\sin\theta(5\cos^2\theta - 1)$$

$$f_4(\theta, \alpha\tau) = -\frac{1}{8}\sqrt{\frac{5}{143}}[18\sin(6\alpha\tau) + 21\sin(12\alpha\tau) + 4\sin(18\alpha\tau) - 18\sin(24\alpha\tau)] \times \sin 2\theta(1 + 7\cos 2\theta)$$

$$f_5(\theta, \alpha\tau) = -\frac{1}{64}\sqrt{\frac{15}{13}}[5 + 4\cos(6\alpha\tau) - 7\cos(12\alpha\tau) - 8\cos(18\alpha\tau) + 6\cos(24\alpha\tau)] \times \sin\theta[15 + 28\cos 2\theta + 21\cos 4\theta]$$

$$f_6(\theta, \alpha\tau) = \frac{7}{128}\sqrt{\frac{3}{55}}[8\sin(6\alpha\tau) + 2\sin(12\alpha\tau) - 8\sin(18\alpha\tau)) + 3\sin(24\alpha\tau)] \times \sin 2\theta(19 + 12\cos 2\theta + 33\cos 4\theta)$$

$$f_7(\theta, \alpha\tau) = \frac{7}{512\sqrt{7293}}[25 - 6\cos(6\alpha\tau) - 48\cos(12\alpha\tau) + 38\cos(18\alpha\tau) - 9\cos(24\alpha\tau)]\sin\theta(350 + 675\cos 2\theta + 594\cos 4\theta + 429\cos 6\theta)$$

$$f_8(\theta, \alpha\tau) = -\frac{3}{2048\sqrt{175}}[84\sin(6\alpha\tau) - 84\sin(12\alpha\tau) + 36\sin(18\alpha\tau) - \sin(24\alpha\tau)]\sin 2\theta(178 + 869\cos 2\theta + 286\cos 4\theta + 715\cos 6\theta)$$

$$f_9(\theta, \alpha\tau) = -\frac{3}{16384}\sqrt{\frac{5}{2431}} \times [105 - 168\cos(6\alpha\tau) + 84\cos(12\alpha\tau) - 24\cos(18\alpha\tau) + 3\cos(24\alpha\tau)] \times \sin\theta(2205 + 4312\cos 2\theta + 4004 \times \cos 4\theta + 3432\cos 6\theta + 2431\cos 8\theta). \quad [A22]$$

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