

Phonon-Assisted Spin Diffusion in Solids

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The spin flip-flop transition rate is calculated for the case of spectral spin diffusion within a system of dipolarly coupled spins in a solid where the lattice vibrations are present. Long-wavelength acoustic phonons time-modulate the interspin distance r_{ij} and enhance the transition rate via the change of the $1/r_{ij}^3$ term in the coupling dipolar Hamiltonian. The phonon-assisted spin diffusion rate is calculated by the golden rule in the Debye approximation of the phonon density of states. The coupling of the spins to the phonons introduces temperature dependence into the transition rate, in contrast to the spin diffusion in a rigid lattice, where the rate is temperature-independent. The direct (one-phonon absorption or emission) processes introduce a linear temperature dependence into the rate at temperatures not too close to $T = 0$. Two-phonon processes introduce a more complicated temperature dependence that again becomes simple analytical for temperatures higher than the Debye temperature, where the rate is proportional to T^2 , and in the limit $T \rightarrow 0$, where the rate varies as T^7 . Raman processes (one-phonon absorption and another phonon emission) dominate by far the phonon-assisted spin flip-flop transitions. © 2000 Academic Press

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I. INTRODUCTION

The concept of spin diffusion was introduced by Bloembergen (1, 2) in order to describe transport of spin polarization between spatially remote spins inside a rigid crystalline lattice. Spin diffusion provides a basis for understanding numerous phenomena in solid-state magnetic resonance like relaxation by paramagnetic impurities (3), dynamic nuclear polarization by Overhauser and solid-state effects (3), electron-nuclear double resonance (4) (ENDOR), and cross polarization in the rotating frame using Hartmann–Hahn matching or adiabatic demagnetization and remagnetization (4). In addition, spin diffusion also provides information about the spatial proximity of atoms in solids in a two-dimensional exchange NMR spectroscopy (5).

Despite the fact that the exchange of spin polarization between remote spins involves a single physical process, determined by the flip-flop term of the magnetic dipole–dipole

interaction (the term B in the dipolar “alphabet”), two kinds of spin diffusion have been introduced in the literature (6, 7). The first is the transport of spin polarization between spatially separated equivalent spins with identically spaced energy levels, so that the total energy of a given flip-flop process is conserved within the given spin pair. This kind of spin diffusion is named “spatial” spin diffusion and can take place within an isolated system of dipolarly coupled spins, not coupled further to an extraneous dipolar reservoir of another spin species or to a crystalline lattice. The spatial spin diffusion represents a pure quantum phenomenon, which is temperature-independent and proceeds also at $T = 0$.

In contrast to spatial spin diffusion, which takes place between equivalent spins only, the polarization exchange between nonequivalent spatially remote spins (that possess different resonance frequencies) was named “spectral” spin diffusion. There the polarization exchange again occurs through the same spin flip-flop process, but there is a mismatch between the spacings of energy levels of the spins involved, so that the spin energy is not conserved in a flip-flop transition. One possible way to satisfy the energy conservation is a dipolar coupling to an extraneous spin reservoir (6, 7). There the total physical system consists of two or more nuclear spin subsystems. One of them contains the resonant spins, whereas the other spins are “passive” and do not participate directly in the exchange process but supply the energy needed to transfer the polarization between the nonequivalent resonant spins. Another possible way to satisfy the energy conservation is via the multiple-quantum spin flips (8). In both cases one deals again with purely quantum effects that do not involve coupling of the spins to the lattice, so that the flip-flop transition rate is temperature-independent and different from zero also at $T = 0$.

Both spatial and spectral spin diffusion processes described above are characterized by temperature-independent rate constants, reflecting the fact that the spin flip-flop transitions are performed within the spin subsystem only, without coupling to the lattice. However, in solids with a well-defined crystalline lattice, lattice vibrations can affect significantly the spin-diffusion rate. The strength of the dipolar spin Hamiltonian depends on the distance between the spin pair as $1/r^3$. Longitudinal

acoustic phonons time-modulate this distance in a harmonic way so that the distance is reduced in a part of the cycle, resulting in an enhancement of the spin diffusion rate. Such a phonon-assisted process should yield a spin diffusion rate that depends on temperature, as a consequence of the coupling of spins to the lattice.

In this paper we present a theoretical description of the temperature-dependent phonon-assisted spin diffusion in solids, where the long-wavelength longitudinal acoustic phonons can propagate through the crystalline lattice. The case of spectral spin diffusion is considered where the energy mismatch of a given flip-flop transition is compensated by the phonon field. The lattice is treated quantum mechanically as a set of independent harmonic oscillators in the Debye approximation. The spin-diffusion rate is calculated in first-order perturbation by the golden rule, and temperature-dependent contributions to the total rate are derived. The calculation follows steps similar to those for the derivation of the magnetic spin-lattice relaxation model by spin-phonon coupling developed for electronic spins by Waller (9) and extended to nuclear spins by Abragam (10).

The motivation for this work came from recent studies of slow dynamic processes in the $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$ proton glass family by two-dimensional (2D) NMR exchange spectroscopy (11, 12) and NMR spin-lattice relaxation (13). The NMR exchange rate and the spin-lattice relaxation rate in proton glasses are believed to be determined by the motion of deuterons in hydrogen bonds. The two rates were found to be strongly temperature-dependent at high temperatures, whereas they became weakly temperature-dependent at low temperatures. This was interpreted as a transition from classical thermally activated hopping motion to quantum tunneling within hydrogen bonds. However, a weak temperature-dependence of both rate constants could originate also from spin-diffusion effects, provided the coupling of spins to the lattice is taken into account.

Another motivation for this work came from the more general, long-existing problem of spectrum analysis in the 2D exchange NMR spectroscopy. The atomic exchange in real space (the chemical exchange) and the exchange of nuclear spin polarization between spatially fixed nuclei (spin diffusion) produce identical cross peaks in the 2D spectrum and cannot be discriminated directly from the 2D exchange spectra. The discrimination of the two effects is usually based on the assumption that the chemical exchange rate depends on temperature but is independent of the frequency separation between the exchanging resonance lines, whereas the spin diffusion rate behaves in the opposite way, depending on the separation but being temperature-independent. Recognizing that spin diffusion might be a temperature-dependent phenomenon makes the above criterion questionable.

Another point to mention is that the temperature-independent spin diffusion can exist only in spin systems with negligible coupling of spins to the lattice. In solids this coupling generally cannot be neglected and the introduction of the lattice

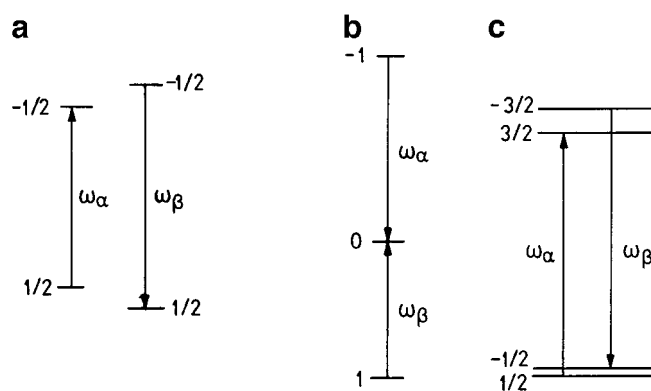


FIG. 1. Some representative situations of the double-spin transitions between the levels with similar transition frequencies, induced by the flip-flop term of the dipolar Hamiltonian. The α and β transitions take place simultaneously on two neighboring spins: (a) two identical spins, $I = \frac{1}{2}$, with different chemical shifts; (b) quadrupole-perturbed $I = 1$ spin in a high magnetic field; (c) quadrupolar $I = \frac{3}{2}$ nucleus with a small Zeeman perturbation. In the double transition the spin energy is not conserved.

as a thermal bath immediately introduces temperature dependence into the spin diffusion rate. The same is true for liquids where molecular vibrations can play the role of lattice vibrations. The temperature-dependent spin diffusion should thus appear more as a rule than as the exception.

II. THE COUPLING HAMILTONIAN

We consider an ensemble of spins with a spin quantum number I and gyromagnetic ratio γ_I . The Hamiltonian of the total system, consisting of spins in a magnetic field and the lattice, is

$$H = H_0 + H_{\text{ph}} + H_{\text{int}}. \quad [1]$$

Here, $H_0 = \sum_i H_{0i}$ is the sum of single-spin Hamiltonians in the absence of spin-spin interactions, comprising the Zeeman, chemical shift, and electric quadrupolar terms. We assume that the magnetic quantum numbers m_i of individual spins are good quantum numbers, so that H_{0i} defines a set of energy levels $|m_i\rangle$ for each spin via the relation $H_{0i}|m_i\rangle = E_{m_i}|m_i\rangle$. The details of the complete energy-level diagram need not be specified for our purpose. The only constraint is that there should exist two transitions within this level manifold (that we shall call α and β), which have similar transition frequencies ω_α and ω_β with the difference $\Delta = \omega_\alpha - \omega_\beta$. We shall further assume in our choice of the interaction Hamiltonian that the α and β transitions correspond to single-quantum ($|\Delta m| = 1$) transitions. Examples of the above situation are displayed in Fig. 1. This can be, e.g., two identical $I = \frac{1}{2}$ spins with different chemical shifts, a quadrupole-perturbed $I = 1$ spin in a high magnetic field or a quadrupolar $I = \frac{3}{2}$ nucleus with a small

Zeeman perturbation, to mention just a few of the many possible situations.

The lattice Hamiltonian H_{ph} is described in terms of lattice vibrations (phonons). We restrict to the case where the frequency mismatch Δ lies within the acoustic phonon bandwidth so that the high-frequency optical phonons can be neglected. We consider the longitudinal acoustic phonons only, as only these are able to change the relative distances between the spins. The theory of a harmonic crystal yields H_{ph} in the form

$$H_{\text{ph}} = \sum_{\vec{k}} \hbar \omega_{\vec{k}} \left(b_{\vec{k}}^{\dagger} b_{\vec{k}} + \frac{1}{2} \right), \quad [2]$$

where \vec{k} and $\omega_{\vec{k}} = c|\vec{k}|$ are the phonon wave vector and frequency, c is the speed of sound, and $b_{\vec{k}}^{\dagger}$ and $b_{\vec{k}}$ are the usual phonon creation and annihilation operators.

The coupling between the spins is taken in the form of the dipole–dipole interaction, which is considered to be a small perturbation to H_0 . For a pair of spins i and j in a rigid lattice, separated by a distance $R_{ij} = |\vec{R}_{ij}| = |\vec{R}_i - \vec{R}_j|$, we write the part of the interaction Hamiltonian relevant for the flip-flop transitions as

$$H_{\text{int}}^{(0)} = -\frac{1}{4} \frac{\gamma^2 \hbar^2}{R_{ij}^3} (1 - 3 \cos^2 \theta_{ij}) (I_i^{\dagger} I_j^{-} + I_i^{-} I_j^{\dagger}). \quad [3]$$

Here, θ_{ij} is the angle between the vector joining the two spins and the z -axis (taken in the direction of the external magnetic field).

In the presence of lattice vibrations, we replace the rigid lattice position \vec{R}_i by

$$\vec{r}_i = \vec{R}_i + \vec{u}_i, \quad [4]$$

where \vec{u}_i is a time- and space-dependent displacement. Assuming that the displacement difference $|\vec{u}_i - \vec{u}_j|$ of the two neighboring spins is small compared to their distance R_{ij} , we expand the factor r_{ij}^{-3} in power series up to the quadratic term and get

$$\begin{aligned} \frac{1}{r_{ij}^3} = \frac{1}{R_{ij}^3} \left\{ 1 - \frac{3(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}}{R_{ij}^2} \right. \\ \left. + \frac{15}{2} \frac{[(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}]^2}{R_{ij}^4} - \frac{3}{2} \frac{(\vec{u}_i - \vec{u}_j)^2}{R_{ij}^2} \right\}. \quad [5] \end{aligned}$$

The interaction Hamiltonian can now be written as a sum of three terms,

$$H_{\text{int}} = H_{\text{int}}^{(0)} + H_{\text{int}}^{(1)} + H_{\text{int}}^{(2)}, \quad [6]$$

with

$$H_{\text{int}}^{(1)} = -H_{\text{int}}^{(0)} \frac{3(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}}{R_{ij}^2} \quad [7a]$$

and

$$H_{\text{int}}^{(2)} = H_{\text{int}}^{(0)} \left\{ \frac{15}{2} \frac{[(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}]^2}{R_{ij}^4} - \frac{3}{2} \frac{(\vec{u}_i - \vec{u}_j)^2}{R_{ij}^2} \right\}. \quad [7b]$$

The Hamiltonian of Eq. [6] causes double spin transitions like those shown in Fig. 1, where the transition α on one spin is accompanied by a simultaneous transition β on another, spatially remote spin.

The interaction Hamiltonian can be put in a form more appropriate for calculations by writing the displacement vector \vec{u} in a normal coordinate expansion

$$\vec{u} = \sum_{\vec{k}} \sqrt{\frac{\hbar}{2MN\omega_{\vec{k}}}} \vec{e}_{\vec{k}} e^{i\vec{k} \cdot \vec{R}} (b_{\vec{k}} + b_{-\vec{k}}^{\dagger}). \quad [8]$$

Here N is the number of normal modes, M is the ionic mass, and $\omega_{\vec{k}}$ and $\vec{e}_{\vec{k}}$ denote the frequency and the polarization vector of a classical normal mode with a wave vector \vec{k} . We dropped the polarization index s as we are considering the longitudinal acoustic phonons only.

The phonon-dependent parts of the interaction Hamiltonian contain a scalar product $(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}$ that is non-zero only if the displacement vector has a component in the direction of the interspin vector \vec{R}_{ij} . Only such phonons can produce a significant change of the distance between the spins. The change of the distance by the atomic displacements in the direction perpendicular to \vec{R}_{ij} is much smaller and can be to a good approximation neglected when we are considering the fluctuations of r_{ij}^{-3} . However, the perpendicular displacements shall induce fluctuations of the $\cos \theta$ term in the dipolar Hamiltonian, which can also affect the spin diffusion rate. We shall comment on this point under Discussion.

We define the angle between \vec{R}_{ij} and the wave vector \vec{k} as ϕ_{ij} (recall that since we are dealing with longitudinal acoustic phonons, the direction of \vec{k} is the same as the direction of the polarization vector $\vec{e}_{\vec{k}}$) and write

$$(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij} = |\vec{u}_i - \vec{u}_j| R_{ij} \cos \phi_{ij} = (\vec{u}_i - \vec{u}_j)_{\parallel} R_{ij}. \quad [9]$$

Here, $(\vec{u}_i - \vec{u}_j)_{\parallel} = |\vec{u}_i - \vec{u}_j| \cos \phi_{ij}$ is the component of the displacement in the direction of the interspin vector \vec{R}_{ij} . In the long wavelength limit we assume that \vec{u} does not vary appreciably over the interatomic distances and replace a component such as $(\vec{u}_i - \vec{u}_j)_{\parallel}$ by its first-order expansion

$$(\tilde{u}_i - \tilde{u}_j)_\parallel = R_{ij} \frac{\partial u_\parallel}{\partial x_\parallel}, \quad [10]$$

where the x_\parallel axis of the coordinate system was chosen parallel to the vector \tilde{R}_{ij} . Equation [8] now yields

$$\frac{\partial u_\parallel}{\partial x_\parallel} = i \cos^2 \phi_{ij} \sum_{\vec{k}} \sqrt{\frac{\hbar \omega_{\vec{k}}}{2MNC^2}} e^{i\vec{k}\cdot\tilde{R}} (b_{\vec{k}} + b_{-\vec{k}}^+), \quad [11]$$

so that Eqs. [7a, 7b] can be rewritten as

$$H_{\text{int}}^{(1)} = -3H_{\text{int}}^{(0)} \frac{\partial u_\parallel}{\partial x_\parallel} \quad [12a]$$

and

$$H_{\text{int}}^{(2)} = H_{\text{int}}^{(0)} \left[6 \left(\frac{\partial u_\parallel}{\partial x_\parallel} \right)^2 - \frac{3}{2} \frac{(\tilde{u}_i - \tilde{u}_j)_\perp^2}{R_{ij}^2} \right] \approx 6H_{\text{int}}^{(0)} \left(\frac{\partial u_\parallel}{\partial x_\parallel} \right)^2, \quad [12b]$$

where—as stated above—the effect of the perpendicular displacement component $(\tilde{u}_i - \tilde{u}_j)_\perp$ in Eq. [12b] can be neglected. The terms $H_{\text{int}}^{(1)}$ and $H_{\text{int}}^{(2)}$ induce spin flip-flop transitions via one-phonon and two-phonon processes, respectively.

III. PHONON-ASSISTED SPIN DIFFUSION RATE

The transition rate for a combined α , β transition, taking place on two different spins in the presence of a phonon field, will now be calculated by the golden rule. Due to the limited validity of the golden rule, this treatment is an approximate one. A more exact treatment of the transition rate, like that given in Ref. (7), becomes hopelessly complicated in the presence of the lattice Hamiltonian. The rate will be calculated by the first-order formula

$$w_{12} = \frac{2\pi}{\hbar} \sum_n |\langle 2, n | H_{\text{int}} | 1, n_0 \rangle|^2 \delta(E_{2,n} - E_{1,n_0}). \quad [13]$$

Here $|1, n_0\rangle$ and $|2, n\rangle$ represent the initial and final states of the combined spin–phonon system, respectively (1, 2 refer to the spin states and n, n_0 denote the phonon states), and the summation is made over the phonon states.

1. One-Phonon (Direct) Processes

The Hamiltonian $H_{\text{int}}^{(1)}$ of Eq. [12a] contains single-phonon creation and annihilation operators that permit an absorption or emission of a single phonon. It thus describes one-phonon (direct) processes.

a. one-phonon absorption. We assume that the spin i undergoes a transition $m_i \rightarrow m_i + 1$ (transition α) and the spin

j undergoes a transition $m_j \rightarrow m_j - 1$ (transition β), with the frequency difference $\Delta = \omega_\alpha - \omega_\beta > 0$. Phonon states are characterized by a mean number of phonons $n_{\vec{k}}$ of a given wave vector \vec{k} present at a temperature T :

$$n_{\vec{k}} = \frac{1}{\exp(\hbar\omega_{\vec{k}}/k_B T) - 1}. \quad [14]$$

A given phonon state will be denoted as $|n_{\vec{k}}\rangle$. The initial state of the total system is thus $|1, n_0\rangle = |m_i, m_j, n_{\vec{k}}\rangle$ and the final state is $|2, n\rangle = |m_i + 1, m_j - 1, n_{\vec{k}} - 1\rangle$. Equation [13] is now written as

$$w_{12} = 9 \cdot \frac{2\pi}{\hbar^2} \sum_n \left| \langle m_i + 1, m_j - 1 | H_{\text{int}}^{(0)} | m_i, m_j \rangle \right. \\ \left. \times \left\langle n_{\vec{k}} - 1 \left| \frac{\partial u_\parallel}{\partial x_\parallel} \right| n_{\vec{k}} \right\rangle \right|^2 \delta(\Delta - \omega_{\vec{k}}). \quad [15]$$

We write the matrix element of $H_{\text{int}}^{(0)}$ in an abbreviated notation as

$$|\langle H_{\text{int}}^{(0)} \rangle_{m_i, m_j}^2 = |\langle m_i + 1, m_j - 1 | H_{\text{int}}^{(0)} | m_i, m_j \rangle|^2$$

and get

$$|\langle H_{\text{int}}^{(0)} \rangle_{m_i, m_j}^2 = \frac{1}{16} \frac{\gamma_I^4 \hbar^4}{R_{ij}^6} (1 - 3 \cos^2 \theta_{ij})^2 \\ \times [I(I+1) - m_i(m_i+1)] \\ \times [I(I+1) - m_j(m_j-1)]. \quad [16]$$

The phonon matrix element is obtained using the relations $b_{\vec{k}}^+ |n_{\vec{k}}\rangle = \sqrt{n_{\vec{k}} + 1} |n_{\vec{k}} + 1\rangle$ and $b_{\vec{k}} |n_{\vec{k}}\rangle = \sqrt{n_{\vec{k}}} |n_{\vec{k}} - 1\rangle$ as

$$\left| \left\langle n_{\vec{k}} - 1 \left| \frac{\partial u_\parallel}{\partial x_\parallel} \right| n_{\vec{k}} \right\rangle \right|^2 = \cos^4 \phi_{ij} \frac{\hbar \omega_{\vec{k}}}{2MNC^2} n_{\vec{k}}. \quad [17]$$

The summation over the phonon states is made in two steps by summing first over the directions of the wave vectors \vec{k} and then over the phonon frequencies $\omega_{\vec{k}}$. We assume for simplicity that the directions of \vec{k} are distributed isotropically in space and average the $\cos^4 \phi_{ij}$ term over the sphere. We get $(4\pi)^{-1} \int_0^\pi d\Omega \cos^4 \phi_{ij} = \frac{1}{5}$. The summation over $\omega_{\vec{k}}$ is replaced by an integration over the Debye density of states,

$$\sum_{\omega_{\vec{k}}} \rightarrow \int_0^{\omega_D} d\omega_{\vec{k}} \rho(\omega_{\vec{k}}) \quad \text{with} \quad \rho(\omega_{\vec{k}}) = \frac{3N\omega_{\vec{k}}^2}{\omega_D^3}.$$

Here, ω_D represents the Debye cutoff frequency that is related

to the Debye temperature θ_D by $\hbar\omega_D = k_B\theta_D$. After integration, Eq. [15] becomes

$$w_{12} = \frac{27\pi}{5\hbar} |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{Mc^2} \left(\frac{\Delta}{\omega_D} \right)^3 \frac{1}{\exp(\hbar\Delta/k_B T) - 1}. \quad [18]$$

The one-phonon absorption rate w_{12} vanishes for $T \rightarrow 0$, reflecting the fact that there are no phonons left at zero temperature. For $\hbar\Delta \ll k_B T$ (the condition that will be met in spectral spin diffusion at practically all temperatures, as the spacing of the resonance lines $\Delta/2\pi$ is of the order of kHz, whereas $k_B T/h$ amounts to 20 MHz at a temperature as low as 1 mK), one is allowed to replace $[\exp(\hbar\Delta/k_B T) - 1]^{-1}$ in Eq. [18] by $k_B T/\hbar\Delta$, so that the rate is directly proportional to the temperature; $w_{12} \propto T$.

b. One-phonon emission. In a reverse transition $m_i + 1 \rightarrow m_i$ and $m_j - 1 \rightarrow m_j$, the energy difference Δ is negative, so that one phonon has to be emitted to satisfy the energy conservation. The initial state of the system is now $|1, n_0\rangle = |m_i + 1, m_j - 1, n_{\bar{k}}\rangle$, and the final state is $|2, n\rangle = |m_i, m_j, n_{\bar{k}} + 1\rangle$. The calculation of the one-phonon emission rate w_{21} proceeds in the same way as before. There one encounters the phonon matrix element of the form

$$\left| \left\langle n_{\bar{k}} + 1 \left| \frac{\partial u_{\parallel}}{\partial x_{\parallel}} \right| n_{\bar{k}} \right\rangle \right|^2 = \cos^4 \phi_{ij} \frac{\hbar\omega_{\bar{k}}}{2MNC^2} (n_{\bar{k}} + 1), \quad [19]$$

yielding

$$w_{21} = \exp(\hbar\Delta/k_B T) w_{12}. \quad [20]$$

The one-phonon absorption and emission rates thus obey detailed balance principle $w_{12}/w_{21} = \exp(-\hbar\Delta/k_B T)$. The emission rate w_{21} is non-zero also at $T \rightarrow 0$, reflecting the fact that the spontaneous one-phonon emission can occur also at $T = 0$. However, due to the validity of the inequality $\hbar\Delta \ll k_B T$ at practically all temperatures (except in the close vicinity of $T = 0$), one can replace $\exp(\hbar\Delta/k_B T)[\exp(\hbar\Delta/k_B T) - 1]^{-1}$ in Eq. [20] again by $k_B T/\hbar\Delta$, so that the one-phonon emission rate is also directly proportional to the temperature; $w_{21} \propto T$.

The total one-phonon flip-flop transition rate $w_{ij}^{(1)}$ of a given pair of spins i and j is obtained by summing up the absorption and emission rates,

$$\begin{aligned} w_{ij}^{(1)} &= w_{12} + w_{21} \\ &= \frac{27\pi}{5\hbar} |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{Mc^2} \left(\frac{\Delta}{\omega_D} \right)^3 \frac{2k_B T}{\hbar\Delta}. \end{aligned} \quad [21]$$

The corresponding one-phonon spin diffusion rate is obtained by summing the contributions from all spins j that interact dipolarly with the given spin i

$$w^{(1)} = \sum_j w_{ij}^{(1)}. \quad [22]$$

In the calculation of $w^{(1)}$ one encounters the term $\sum_j |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2$ that can be conveniently expressed in terms of the second moment (14)

$$M_2 = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \sum_j \frac{(1 - 3 \cos^2 \theta_{ij})^2}{R_{ij}^6}. \quad [23]$$

Using Eq. [16] and defining

$$f = \frac{[I(I+1) - m_i(m_i+1)][I(I+1) - m_j(m_j-1)]}{I(I+1)}, \quad [24]$$

one gets

$$\sum_j |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 = \frac{\hbar^2}{12} M_2 f \quad [25]$$

so that the one-phonon spin diffusion rate can be written as

$$w^{(1)} = \frac{9\pi}{10} M_2 f \frac{1}{Mc^2} \left(\frac{\Delta}{\omega_D} \right)^3 \frac{k_B T}{\Delta}. \quad [26]$$

A characteristic feature of $w^{(1)}$ is its linear dependence on temperature. It thus represents a temperature-dependent contribution to the total spin-diffusion rate via the direct (one-phonon) absorption and emission processes.

2. Two-Phonon Processes

The Hamiltonian $H_{\text{int}}^{(2)}$ of Eq. [12b] contains quadratic forms of the phonon creation and annihilation operators and describes two-phonon processes. There are four such processes, a two-phonon absorption, a two-phonon emission, and two Raman processes (the absorption of one phonon and the emission of another, and the reverse process). We calculate the transition rates again by Eq. [13].

a. Two-phonon absorption. The initial state of the system is here $|1, n_0\rangle = |m_i, m_j, n_{\bar{k}}, n_{\bar{k}'}\rangle$, and the final state is $|2, n\rangle = |m_i + 1, m_j - 1, n_{\bar{k}} - 1, n_{\bar{k}'} - 1\rangle$. In the calculation of the matrix element of $H_{\text{int}}^{(2)}$ one encounters a phonon matrix element

$$\begin{aligned} & \left| \left\langle n_{\bar{k}} - 1, n_{\bar{k}'} - 1 \left| \left(\frac{\partial u_{\parallel}}{\partial x_{\parallel}} \right)^2 \right| n_{\bar{k}}, n_{\bar{k}'} \right\rangle \right|^2 \\ &= \left(\frac{\hbar}{2MNC^2} \cos^4 \phi_{ij} \right)^2 \omega_{\bar{k}} \omega_{\bar{k}'} n_{\bar{k}} n_{\bar{k}'}. \end{aligned} \quad [27]$$

In the summation over the phonon states we again first average over the spherically isotropic distribution of \vec{k} directions and next sum over the frequency spectrum of both phonons. We get

$$w_{12}^{(2abs)} = 18\pi |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \int d\omega_{\vec{k}} \int d\omega_{\vec{k}'} \omega_{\vec{k}}^3 \omega_{\vec{k}'}^3 \\ \times \frac{1}{[\exp(\hbar\omega_{\vec{k}}/k_B T) - 1]} \\ \times \frac{1}{[\exp(\hbar\omega_{\vec{k}'}/k_B T) - 1]} \delta(\Delta - \omega_{\vec{k}} - \omega_{\vec{k}'}). \quad [28]$$

Performing the integration over the δ -function, we get

$$w_{12}^{(2abs)} = 18\pi |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \int_0^\Delta d\omega (\Delta - \omega)^3 \omega^3 \\ \times \frac{1}{\{\exp[\hbar(\Delta - \omega)/k_B T] - 1\}} \\ \times \frac{1}{[\exp(\hbar\omega/k_B T) - 1]}. \quad [29]$$

Here the limits of integration $[0, \Delta]$ reflect the fact that only those phonons from the spectrum participate in the two-phonon absorption process whose frequencies satisfy the energy-conserving condition $\omega_{\vec{k}} + \omega_{\vec{k}'} = \Delta$. Since Δ is small compared to ω_D , only a small part of the phonon spectrum is involved.

b. Raman process. In the Raman process, a phonon \vec{k}' is absorbed whereas another phonon \vec{k} is emitted. The initial and final states are here $|1, n_0\rangle = |m_i, m_j, n_{\vec{k}}, n_{\vec{k}'}\rangle$ and $|2, n\rangle = |m_i + 1, m_j - 1, n_{\vec{k}} + 1, n_{\vec{k}'} - 1\rangle$. We assume that the absorbed phonon has higher energy than the emitted one so that the energy conservation is given by $\omega_{\vec{k}'} = \omega_{\vec{k}} + \Delta$. A straightforward calculation yields the rate for this Raman process (denoted as R1) as

$$w_{12}^{(R1)} = 18\pi |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \int_\Delta^{\omega_D} d\omega (\Delta - \omega)^3 \omega^3 \\ \times \frac{1}{\{\exp[\hbar(\Delta - \omega)/k_B T] - 1\}} \\ \times \frac{1}{[\exp(\hbar\omega/k_B T) - 1]}. \quad [30]$$

Equation [30] is exactly the same as Eq. [29], except for the limits of integration which extend here from Δ to ω_D (note that since $\omega > \Delta$, the negative sign of $(\Delta - \omega)^3$ in the integral is compensated by the negative sign of the $\{\exp[\hbar(\Delta - \omega)/k_B T] - 1\}^{-1}$ term, so that $w_{12}^{(R1)}$ is positive). The integration limits

$[\Delta, \omega_D]$ demonstrate that in the Raman process the phonons from the whole spectrum participate, with the restriction that the difference in frequencies of the two phonons involved equals Δ . Since $\Delta \ll \omega_D$, practically all phonons from the spectrum are involved, so that the Raman rate should be much larger than the two-phonon absorption rate.

Since the rates $w_{12}^{(2abs)}$ and $w_{12}^{(R1)}$ differ only in the integration limits, we can combine these two terms into a sum rate

$$w_{12}^{(2abs)} + w_{12}^{(R1)} \\ = 18\pi |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \int_0^{\omega_D} d\omega (\Delta - \omega)^3 \omega^3 \\ \times \frac{1}{\{\exp[\hbar(\Delta - \omega)/k_B T] - 1\}} \cdot \frac{1}{[\exp(\hbar\omega/k_B T) - 1]}, \quad [31]$$

where the integration now extends from 0 to ω_D .

c. Two-phonon emission rate and the inverse Raman rate. In the reverse spin transitions $m_i + 1 \rightarrow m_i$ and $m_j - 1 \rightarrow m_j$, the energy difference Δ is negative. In order to satisfy the energy conservation, two phonons are emitted (a two-phonon emission process) or a phonon \vec{k} is emitted and \vec{k}' is absorbed, with the energy of the emitted phonon higher than that of the absorbed one (the reverse Raman process). The initial state is $|1, n_0\rangle = |m_i + 1, m_j - 1, n_{\vec{k}}, n_{\vec{k}'}\rangle$, and the final state for the two-phonon emission is $|2, n\rangle = |m_i, m_j, n_{\vec{k}} + 1, n_{\vec{k}'} + 1\rangle$ with the energy conservation condition $\omega_{\vec{k}} + \omega_{\vec{k}'} = \Delta$, whereas for the reverse Raman process the final state is $|2, n\rangle = |m_i, m_j, n_{\vec{k}} + 1, n_{\vec{k}'} - 1\rangle$ with $\omega_{\vec{k}'} = \omega_{\vec{k}} - \Delta$. Performing the same calculation as before, we get the sum of the two-phonon emission rate $w_{21}^{(2em)}$ and the reverse Raman rate $w_{21}^{(R2)}$ as

$$w_{21}^{(2em)} + w_{21}^{(R2)} = \exp(\hbar\Delta/k_B T) [w_{12}^{(2abs)} + w_{12}^{(R1)}]. \quad [32]$$

The total two-phonon transition rate $w_{ij}^{(2)}$ of the pair of spins i and j is obtained by summing up the rates of all four two-phonon processes. We get

$$w_{ij}^{(2)} = w_{12}^{(2abs)} + w_{12}^{(R1)} + w_{21}^{(2em)} + w_{21}^{(R2)} \\ = 18\pi |\langle H_{\text{int}}^{(0)} \rangle|_{m_i, m_j}^2 \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} [1 + \exp(\hbar\Delta/k_B T)] \\ \times \int_0^{\omega_D} d\omega (\Delta - \omega)^3 \omega^3 \frac{1}{\{\exp[\hbar(\Delta - \omega)/k_B T] - 1\}} \\ \times \frac{1}{[\exp(\hbar\omega/k_B T) - 1]}. \quad [33]$$

It is easy to see that since $\Delta \ll \omega_D$, the rate $w_{ij}^{(2)}$ is essentially

independent of the energy mismatch Δ . Low frequencies $\omega \approx \Delta$ contribute almost negligibly to the integral in Eq. [33], so that it is allowed that we make the $\Delta \rightarrow 0$ approximation, yielding

$$w_{ij}^{(2)} = 18\pi |\langle H_{\text{int}}^{(0)} \rangle_{m_i, m_j}^2| \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \times \int_0^{\omega_D} d\omega \frac{\omega^6}{\cosh(\hbar\omega/k_B T) - 1}. \quad [34]$$

The two-phonon spin diffusion rate is again obtained by summing the contributions from all j spins,

$$w^{(2)} = \sum_j w_{ij}^{(2)}. \quad [35]$$

Using Eq. [25] $w^{(2)}$ can be written as

$$w^{(2)} = \frac{3\pi}{2} \hbar^2 M_2 f \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \times \int_0^{\omega_D} d\omega \frac{\omega^6}{\cosh(\hbar\omega/k_B T) - 1}. \quad [36]$$

The two-phonon rate $w^{(2)}$ thus represents another temperature-dependent contribution to the total spin-diffusion rate. Its dependence on temperature is displayed in Fig. 2. At temperatures much higher than the Debye temperature θ_D (where $k_B T \gg \hbar\omega_D$), $w^{(2)}$ gets a simple temperature dependence. There we may expand the cosh term in Eq. [36] in series, and the resulting integral may be calculated easily, yielding

$$w^{(2)} = \frac{3\pi}{5} \hbar^2 M_2 f \frac{1}{(Mc^2)^2} \frac{1}{\omega_D} \left(\frac{k_B T}{\hbar} \right)^2. \quad [37]$$

In the high-temperature limit $T > \theta_D$ the rate $w^{(2)}$ thus depends on temperature as T^2 . At the other extreme $T \rightarrow 0$, another analytical temperature dependence of $w^{(2)}$ can be derived by introducing $x = \hbar\omega/k_B T$ into Eq. [36]. The upper limit of integration θ_D/T may then be extended to infinity, yielding

$$w^{(2)} = \frac{3\pi}{2} \hbar^2 M_2 f \frac{1}{(Mc^2)^2} \frac{1}{\omega_D^6} \left(\frac{k_B T}{\hbar} \right)^7 \times \int_0^\infty dx \frac{x^6}{\cosh x - 1}. \quad [38]$$

The integral in Eq. [38] is finite so that the rate $w^{(2)}$ varies as T^7 in the limit $T \rightarrow 0$.

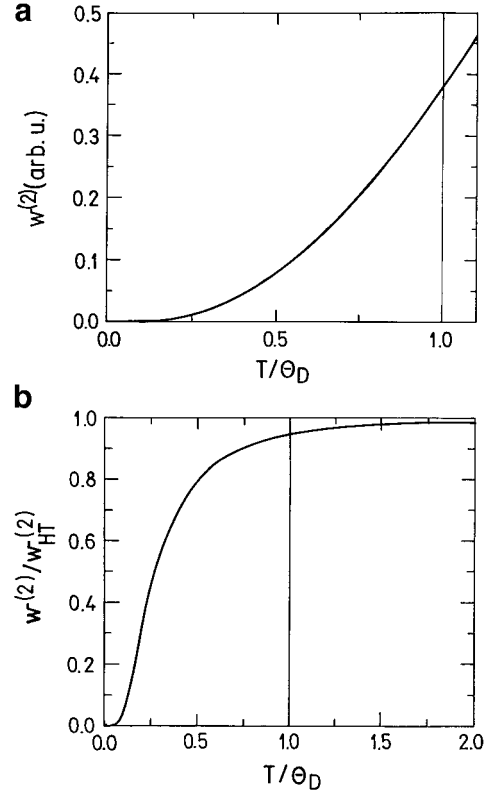


FIG. 2. (a) Temperature dependence of the two-phonon spin diffusion rate $w^{(2)}$ given by Eq. [36] (the normalized integral of that equation is displayed only). (b) The ratio of $w^{(2)}$ (Eq. [36]) and its high-temperature expression given by Eq. [37] (denoted on this graph as $w_{\text{HT}}^{(2)}$) as a function of temperature. This ratio is shown in order to demonstrate the temperature range where the high-temperature expression $w_{\text{HT}}^{(2)}$ is a good approximation to $w^{(2)}$. The two expressions agree to better than 90% at temperatures higher than $T \approx 0.7\theta_D$.

IV. DISCUSSION

The phonon-assisted transition rates $w^{(1)}$ and $w^{(2)}$ represent temperature-dependent contributions to the total spin diffusion rate as a result of coupling of the spin degrees of freedom to the lattice. In a classical picture the temperature-dependence of the rates originates from lattice vibrations that time-modulate the distance between the interacting spin partners and change the $1/r_{ij}^3$ factor in the coupling Hamiltonian, resulting in an enhanced dipolar interaction between the spins. In the one-phonon processes only those phonons from the spectrum are involved whose frequencies equal Δ . In the two-phonon processes, two-phonon absorption and emission involve phonons from an already larger (but still relatively small) part of the spectrum with frequencies between 0 and Δ . The Raman processes, on the other hand, involve phonons from the entire spectrum, extending from 0 to ω_D , so that these processes should be by far dominant at temperatures not too close to $T = 0$. This can readily be seen by calculating the ratio $w^{(1)}/w^{(2)}$ using Eq. [26] and the high-temperature expression Eq. [37].

One gets

$$\frac{w^{(1)}}{w^{(2)}} = \frac{3}{2} \frac{Mc^2}{k_B T} \left(\frac{\Delta}{\omega_D} \right)^2. \quad [39]$$

The factor $Mc^2/k_B T$ is of the order of 10 at room temperature, and since the Debye frequency is typically of the order $\omega_D \approx 10^{13} \text{ s}^{-1}$, whereas Δ is of the order of kHz, the ratio $w^{(1)}/w^{(2)} \ll 1$ is vanishing small. The one-phonon processes may thus be neglected at temperatures not too close to zero. At temperatures close to $T = 0$, however, the one-phonon processes start to dominate over the Raman processes due to the fact that the one-phonon spontaneous emission can still occur at $T = 0$, whereas the Raman processes (where one of the two phonons involved has to be absorbed) vanish due to the vanishing of the phonon occupation number $n_{\vec{k}}$ at $T = 0$. In addition to the one-phonon emission, the two-phonon emission can also occur at $T = 0$, but both these processes result in very small spin diffusion rates. If we are restricted to the temperatures that are not too close to zero, we may expect that the temperature dependence of the total phonon-assisted spin diffusion rate will be determined by that of $w^{(2)}$.

Another point to discuss is the use of the long-wavelength approximation as given by Eq. [10]. This approximation, which rests on the assumption that the phonon-induced atomic displacements \vec{u} do not vary appreciably over an interatomic distance a , is only correct for vibrations of wavelength $\lambda = 2\pi c/\omega$, appreciably larger than the interatomic spacing. The approximation thus breaks down at the upper end of the phonon spectrum when $\omega \approx \omega_D$. Although there is no real justification for this step (performed mainly because of mathematical tractability), one may anticipate the arguments of Abragam (15), who argued in a similar calculation of the phonon-induced NMR spin-lattice relaxation rate that this inconsistency does not appreciably affect the results.

The total spin diffusion rate $1/\tau_{SD}$ is obtained by adding the temperature-dependent contributions $w^{(1)}$ and $w^{(2)}$ to the temperature-independent contribution $w^{(0)}$ that is determined by the term $H_{\text{int}}^{(0)}$ (Eq. [6]) of the interaction Hamiltonian,

$$\frac{1}{\tau_{SD}} = w^{(0)} + w^{(1)} + w^{(2)}. \quad [40]$$

The rate $w^{(0)}$ represents the spin diffusion rate in the absence of coupling of spins to the lattice. In our choice of the main Hamiltonian H_0 , the dipolar interaction between the spins I_i was not taken into account in the calculation of the energy levels, but was treated as a perturbation only that causes flip-flop transitions between the levels. The levels are thus sharp in this approximation, so that in the presence of an energy mismatch Δ there is no overlap between the levels. In real systems such a situation is met in cases where the separation between the exchanging resonance lines is considerably

larger than their widths so that there is no overlap between the lines. The lack of energy conservation then yields $w^{(0)} = 0$ in the above model.

In a more realistic description, the dipolar coupling between the spins I_i , as well as the dipolar coupling of spins I_i to the "passive" extraneous spins S_j , should be taken into account already in the calculation of the energy levels. The levels would then acquire certain widths, and the overlap between the resonance lines would induce a non-zero rate $w^{(0)}$. Here, however, one encounters the problem that the mismatch energy Δ in a spin flip-flop transition can be shared rather arbitrarily between the phonon field and the dipolar reservoir of the passive spins. This is clearly a complicated situation that is not easy to handle in a theoretical model.

An *ad hoc* solution of the above problem can be proposed by adopting the results of Bloembergen (2), where the spin diffusion rate $w^{(0)}$ of the $H_{\text{int}}^{(0)}$ term was derived (again by means of the golden rule) under the assumption of finite linewidths. The resonance lines of the transitions α and β are described by the lineshape functions $g_\alpha(\omega)$ and $g_\beta(\omega)$, respectively, and the rate $w^{(0)}$ is calculated to be

$$w^{(0)} = \frac{1}{12} M_2 f \int d\omega' \int d\omega'' g_\alpha(\omega') g_\beta(\omega'') \delta(\omega' - \omega''), \quad [41]$$

where the integral represents the overlap between the two resonances. This rate vanishes rapidly (exponentially in the case of Gaussian lineshapes) when the frequency separation $\omega_\alpha - \omega_\beta$ of the lines becomes larger than their widths $\Delta\omega_{\alpha,\beta}$.

The above phonon-assisted spin diffusion rates $w^{(1)}$ and $w^{(2)}$ were derived analytically under certain approximations, which made the calculations mathematically tractable. The approximations involve the use of the golden rule, the Debye density of phonon states in a monoatomic crystalline lattice, and the long-wavelength expansion of the atomic displacements. In view of that one should not be too surprised if the magnitudes of $w^{(1)}$ and $w^{(2)}$, estimated from Eqs. [26] and [36], fail in the order of magnitude. The temperature dependence of the rates (linear in T for the one-phonon processes, and T^2 at $T > \theta_D$ and T^7 for $T \rightarrow 0$ for the two-phonon processes) is, on the other hand, typical for phonon-assisted rate processes and hence can be considered as correct. We can estimate the order of magnitude of the two-phonon rate $w^{(2)}$ from Eq. [37] for the ^{87}Rb spin diffusion in ferroelectric RbH_2PO_4 , where the presence of spin diffusion between the ^{87}Rb nuclei was demonstrated unambiguously (16). The ^{87}Rb second moment was determined there to be $M_2 = 6 \times 10^8 \text{ s}^{-2}$, and the Debye temperature in this crystal is known to be about 400 K, yielding $\omega_D \approx 5 \times 10^{13} \text{ s}^{-1}$. Taking $c \approx 3 \times 10^3 \text{ ms}^{-1}$ for the speed of sound, we get at $T = 400 \text{ K}$ the order of magnitude of $w^{(2)} \approx 10^{-8} \text{ s}^{-1}$ that results in astronomically long spin diffusion times. The main reason for the smallness of $w^{(2)}$ is the

Debye frequency ω_D of the order 10^{13} s^{-1} in the denominator of Eq. [37], which essentially kills the rate. The rate $w^{(2)}$ would increase for several orders of magnitude if the ^{87}Rb nuclei were replaced by lighter nuclei with larger magnetic dipole moments, e.g., ^1H . Since $M_2 \propto \gamma^4$, the second moment of protons increases by a factor $M_2(^1\text{H})/M_2(^{87}\text{Rb}) \approx 10^2$. In addition, the mass ratio yields another increase of $[M(^{87}\text{Rb})/M(^1\text{H})]^2 \approx 10^4$, so that the order of magnitude of the rate is increased to $w^{(2)}(^1\text{H}) \approx 10^{-2} \text{ s}^{-1}$. This is already observable in an experiment. The theory of phonon-assisted spin diffusion, presented in this paper, should thus be taken as a starting point toward a more complete theory that should yield better estimates of the magnitudes of the rates. One can, however, expect that the temperature dependence of the rates in such an improved theory will not be much different from the one derived here.

In the above model it was considered that the spin diffusion rate is affected by the lattice vibrations through the fluctuations of the interspin distance r_{ij} only. Phonons can, however, modify the dipolar Hamiltonian also through another effect, i.e., the fluctuations of the $\cos^2\theta$ term. This corresponds to orientation fluctuations of the interspin vector \vec{r}_{ij} with respect to the direction of the magnetic field $\vec{B}_0 = (0, 0, B_0)$. The orientation fluctuations do not influence all spin pairs equally. The $\cos^2\theta$ angular dependence implies that the pairs with orientations of their interspin vectors close to parallel ($\theta \approx 0$) or perpendicular ($\theta \approx \pi/2$) to \vec{B}_0 do not alter their dipolar coupling by the fluctuations in θ due to the very slow change of the $\cos^2\theta$ there. The pairs with orientations $\theta \approx \pi/4$ are, on the other hand, affected significantly, so that the θ fluctuations provide another phonon-assisted temperature-dependent contribution to the total spin diffusion rate.

An interaction Hamiltonian for the combined θ and distance fluctuations can be derived by expanding the term $r_{ij}^{-3}(t)(1 - 3 \cos^2\theta_{ij}(t))$ of the dipolar Hamiltonian in terms of the atomic displacements \vec{u}_i . A calculation similar to that used for the derivation of Eq. [5] yields an expansion up to the linear term in \vec{u} as

$$\begin{aligned} & \frac{1 - 3 \cos^2\theta_{ij}(t)}{r_{ij}^3(t)} \\ & \approx \frac{1 - 3 \cos^2\theta_{ij}}{R_{ij}^3} \left(1 - \frac{3(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}}{R_{ij}^2} \right) \\ & + \frac{6}{R_{ij}^3} \left[\cos^2\theta_{ij} \frac{(\vec{u}_i - \vec{u}_j) \cdot \vec{R}_{ij}}{R_{ij}^2} - \cos\theta_{ij} \frac{u_i^z - u_j^z}{R_{ij}} \right]. \quad [42] \end{aligned}$$

Here, $\cos\theta_{ij}(t) = (\vec{r}_{ij} \cdot (0, 0, 1)/r_{ij}) = (z_{ij}/r_{ij})$ (with $z_{ij} = Z_{ij} + u_i^z - u_j^z$) and $\cos\theta_{ij} = (\vec{R}_{ij} \cdot (0, 0, 1)/R_{ij}) = (Z_{ij}/R_{ij})$ are the time-dependent and static (time-average) values of the cosine term, respectively. The first term on the right-hand side of Eq. [42] originates from the distance fluctuations whereas the θ fluctuations contribute the second term. It is easy to see that the θ fluctuations are zero for $\theta = 0$ and $\pi/2$. For $\theta = \pi/2$

this vanishing is trivial, whereas for $\theta = 0$ the square bracket becomes $X_{ij}(u_i^x - u_j^x) + Y_{ij}(u_i^y - u_j^y)$, that is zero, due to $X_{ij} = Y_{ij} = 0$.

Equation [42] shows that the θ fluctuations might yield a contribution to the total spin diffusion rate comparable to that of the distance fluctuations. Since both kinds of fluctuations depend on the atomic displacements in the same way, their spin flip-flop rate contributions shall exhibit the same temperature dependence. The θ fluctuations will thus basically increase the magnitude of the phonon-assisted spin diffusion rate. Further work is needed to consider this effect in more detail.

V. CONCLUSIONS

Spectral spin diffusion in the presence of acoustic vibrations in a solid-state crystal is a temperature-dependent phenomenon with a relatively simple temperature dependence of the transition rate. Like in any phonon-assisted incoherent phenomenon (e.g., phonon-induced incoherent tunneling), the direct (one-phonon) processes introduce a linear temperature dependence of the rate at temperatures not too close to $T = 0$. Two-phonon processes, on the other hand, introduce a more complicated temperature dependence that again becomes simple analytical in the limits $T > \theta_D$ and $T \rightarrow 0$. Recognizing that the spin diffusion rate can be temperature-dependent somewhat complicates the analysis of the two-dimensional exchange NMR spectra where the effects of chemical exchange and spin diffusion cannot be resolved in a simple way. The discrimination of the two effects is usually based on the assumption that the chemical exchange rate depends on temperature but is independent of the frequency separation of the exchanging resonance lines, whereas the spin diffusion rate behaves in the opposite way, depending on the separation but being independent of temperature. The fact that in a solid both rates are temperature-dependent, but with a markedly different temperature dependence (the linear and quadratic phonon-induced dependence at temperatures not too close to $T = 0$ has to be contrasted with the Arrhenius thermally activated exponential type in the chemical exchange process), may still be used as a criterion to discriminate between the two effects. However, one has to measure the rate experimentally in a rather broad temperature interval and determine its origin from the temperature dependence. The simple fact that the rate is temperature-dependent is not enough to assign it unambiguously to a chemical exchange process. A similar temperature dependence of the spin diffusion rate can be expected also in liquids where internal molecular vibrations play the role of lattice vibrations. The temperature-dependent spin diffusion thus seems to be a rather general phenomenon, occurring more as a rule than as an exception at temperatures not close to the absolute zero.

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