Spin-lattice relaxation of heavy spin-1/2 nuclei in diamagnetic solids: A Raman process mediated by spin-rotation interaction

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We present a theory for the nuclear spin-lattice relaxation of heavy spin-1/2 nuclei in solids, which explains within an order of magnitude the unexpectedly effective lead and thallium nuclear spin-lattice relaxation rates observed in the ionic solids lead molybdate, lead chloride, lead nitrate, thallium nitrate, thallium nitrite, and thallium perchlorate. The observed rates are proportional to the square of the temperature and are independent of magnetic field. This rules out all known mechanisms usually employed to model nuclear spin relaxation in lighter spin-1/2 nuclei. The relaxation is caused by a Raman process involving the interactions between nuclear spins and lattice vibrations via a fluctuating spin-rotation magnetic field. The model places an emphasis on the time dependence of the angular velocity of pairs of adjacent atoms rather than on their angular momentum. Thus the spin-rotation interaction is characterized not in the traditional manner by a spin-rotation constant but by a related physical parameter, the magnetorotation constant, which relates the local magnetic field generated by spin rotation to an angular velocity. Our semiclassical relaxation model involves a frequency-mode description of the spectral density that can directly be related to the mean-square amplitudes and mode densities of lattice vibrations in the Debye model.

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I. INTRODUCTION

We present a detailed theoretical model to explain the results of a significant number of unusual and unanticipated heavy-spin-1/2 nuclear spin-lattice relaxation experiments in crystalline solids. We list results of spin-lattice relaxation-time measurements for all the spin-1/2 nuclei heavier than ^{103}Rh in Table I.[1–15] The unusual experimental results are that the spin-lattice relaxation rates $1/T_1$ of several of these nuclei simultaneously have three properties: First, the relaxation, in the absence of paramagnetic impurities and large-scale molecular motion, is much more efficient than expected on the basis of experience with lighter nuclei in solids. The usual mechanisms (dipolar interactions, J couplings, chemical shifts, etc.) are unable to explain the efficient nuclear spin-lattice relaxation process observed.[15] Second, $1/T_1$ is proportional to the square of the temperature T and, third, $1/T_1$ is independent of the nuclear magnetic resonance (NMR) frequency $\omega_0 = \gamma B_0$, where γ is the nuclear gyromagnetic ratio and B_0 is the applied static magnetic field in an NMR experiment. Properties 2 and 3 are summarized by

$$1/T_1 = AT^2, \quad (1.1)$$

where the coefficient A is independent of ω_0. In this paper we develop a theory of a relaxation mechanism that gives Eq. (1.1) and we apply it to ^{129}Xe, ^{203,205}Tl, and ^{207}Pb by computing approximate values for the proportionality constants A. These are the only three nuclei with published spin-lattice relaxation results in compliance with Eq. (1.1). The temperature dependence and the NMR-frequency dependence (or lack of it) for compounds with the other nuclei shown in Table I have not yet been observed, either because no such measurements have been reported in the literature or because the relaxation process is dominated by another mechanism, such as atomic diffusion (as in the ionic conduc-

tor γ-^{109}Ag$_7$P$_3$S$_{11}$), interactions with paramagnetic impurities (as in ^{111,113}CdMoO$_4$ and ^{111,113}CdI$_2$ where the relaxation is highly nonexponential), or dipole interactions with mobile proton species (as is possibly the case with the ^{199}Hg salts listed in Table I). We have reason to believe that the relaxation mechanism described by Eq. (1.1) is present in most crystalline solids but that it is most often overwhelmed by other more effective relaxation pathways. The examples presented in Table I and the lack of evidence for a T^2 relaxation-rate dependence in lighter nuclei suggest that the size of A is strongly correlated with the atomic weight.

Our group has a long-standing interest in the NMR spectroscopy of heavy nuclei, in particular ^{207}Pb, the heaviest of the spin-1/2 nuclei.[16–19] Recently, we have focused on spin-lattice relaxation of ^{207}Pb and ^{111,113}Cd in ionic solids[4,5,14,15] and have begun projects for ^{119}Sn and ^{199}Hg. The study of heavy-nucleus spin-lattice relaxation is a field in its infancy. $1/T_1$ determinations can often take many days or even weeks of continuous experimentation, and performing the experiments at low and high temperatures provides additional difficulties for making the measurements.

Grutzner *et al.*[15] observed that the behavior expressed in Eq. (1.1) is indicative of a Raman process of nuclear spin-lattice relaxation involving crystal-lattice vibrations.[20–23] They suggested that the spin-rotation coupling associated with the fluctuating reorientations of internuclear vectors is responsible for the relaxation but a quantitative explanation of a specific coupling mechanism was not proposed. In this paper, we propose an explicit spin-rotation relaxation model that predicts relaxation times of the order of those observed experimentally. It invokes assumptions similar to those made by Fitzgerald and coworkers,[6] who provided a model for the nuclear spin-lattice relaxation times of frozen ^{129}Xe, which they observed to range from 30 h at 20 K to 1 h at 110 K.[6] Except at temperatures well below the Debye temperature,

TABLE I. Spin-lattice relaxation times of heavy-element spin-1/2 nuclei in solids.

Nucleus	Compound	T_1 at RT (s)	T dependence	Reference
^{109}Ag	Ag salts	extremely long	–	1 and 2
^{109}Ag	γ-Ag$_7$P$_3$S$_{11}$	30[a]	–	3
^{111,113}Cd	CdMoO$_4$	extremely long[b]	–	4
^{111,113}Cd	CdI$_2$	extremely long[b]	–	5
^{119}Sn	SnF$_2$	50	T^{-2}	5
^{129}Xe	solid Xe	375[c]	T^{-2}	6 and 7
^{183}W	no example found		–	
^{187}Os	no example found		–	
^{195}Pt	no example found		–	
^{199}Hg	Hg$_2$(NO$_3$)$_2$.2H$_2$O	~5	–	8
^{199}Hg	NEt$_4$Na[Hg(CN)$_4$]	8	–	9
^{199}Hg	(NBu$_4$)$_2$[Hg(SCN)$_2$]	29	–	9
^{199}Hg	Hg(CH$_3$COO)$_2$	290	–	9
^{205}Tl	TlNO$_2$	3.5[d]	T^{-2}	10
^{203,205}Tl	TlNO$_3$	8	T^{-2}	11
^{205}Tl	TlClO$_4$	16[e]	T^{-2}	12
^{207}Pb	Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$	1.0	–	13
^{207}Pb	PbO (red)	1.5	–	13
^{207}Pb	PbMoO$_4$	5	T^{-2}	14
^{207}Pb	PbTiO$_3$	7	–	13
^{207}Pb	Pb(NO$_3$)$_2$	8	T^{-2}	15
^{207}Pb	PbZrO$_4$, two sites	4.2, 5.5	–	13
^{207}Pb	PbCl$_2$	10	T^{-2}	14
^{207}Pb	PbSO$_4$	10.2	–	13
^{207}Pb	PbC$_2$O$_4$	20.4	–	13
^{207}Pb	PbO (yellow)	24.8	–	13
^{207}Pb	PbNb$_2$O$_6$, two sites	30, 5.6	–	13
^{207}Pb	Pb$_3$O$_4$, two sites	44, 160	–	13

[a]Relaxation is dominated by ionic diffusion.

[b]Nonexponential relaxation due to paramagnetic impurities was observed; the intrinsic T_1 is longer than 1000 s.

[c]Extrapolated from low temperature results.

[d]The long-decay relaxation component is due to NO$_2^-$ flips and an additional mechanism is given by $1/T_1 = 3.2 \times 10^{-6} T^2$ (T_1 in s, T in K).

[e]Data points plotted in Fig. 7 of Ref. 12 were fit to $1/T_1 = 6.1 \times 10^{-7} T^2 + 0.008$ (T_1 in s, T in K).

those relaxation rates followed the temperature dependence of Eq. (1.1). They were explained quantitatively as being the result of the fluctuation of an internal spin-rotation field generated by lattice vibrations. Our model, though less specific, is applicable to a wider class of solid materials.

One may be surprised by the apparent importance of rotational motions in solid materials lacking obvious rotating substructures. Spin-rotation relaxation in solids akin to the process prevailing in gases has been observed in only very few cases involving nearly unobstructed rotation of structural units. Examples are spin-lattice relaxation of ^{19}F in SF$_6$, SeF$_6$, and TeF$_6$ (Ref. 24) and of ^{13}C in C$_{60}$.[25,26] However, in the compounds listed in Table I, there is no other motion than that of atoms fluctuating about their equilibrium positions by approximately 0.05 Å on a timescale of approximately

10^{-13} s. Yet, if lattice vibrations displace two adjacent atoms separated by 2 Å by that amount in opposite directions perpendicular to their interconnecting vector, that vector is rotated over 0.05 radians, or 3°. In this paper, when we say that a local substructure in a vibrating crystal performs "rotational motion," we are referring to this kind of time-dependent orientational fluctuation. The concept of "rotation" is thus not limited to states of persistent revolutions about a fixed axis (as found in gas molecules), but includes the motion of a structural entity that changes its orientation over any angle (as found in librating molecular groups). The random time dependence of the reorientation implies that the substructure has an angular velocity that fluctuates randomly on a very short time scale. This rotational motion generates a fluctuating magnetic field via the spin-rotation mechanism.

In a solid material, the physical situation for nuclear spin-lattice relaxation resulting in the modulation of an angular velocity is similar to the spin-rotation relaxation in some liquids, where angular-momentum correlation times shorter than 10^{-13} s have been reported.[27–30] In such a liquid, molecular collisions interrupt angular velocities after rotations of much less than 7°.[27,28] An essential difference between these rotations in liquids and the rotation associated with lattice vibrations in solids is that, after a while, the tiny orientational increments in a liquid add up to full molecular revolutions, while in the solid the accumulated angle of rotation remains restricted. However, for spin-rotation relaxation, this distinction is irrelevant because fluctuations of the orientational velocity, rather than of the orientation itself, are important. In this sense, the fluctuations of the spin-rotation interaction in solids are very similar to those in some liquids.

In the following sections we develop, from first principles, a theory of nuclear spin-lattice relaxation mediated by magnetic coupling of the nuclear spins to lattice vibrations. In contrast to the conventional approach, which is based on a quantum-mechanical phonon model of the vibrations,[20–23] we describe the lattice vibrations classically. In Sec. II we present the semiclassical theory in a form convenient for incorporation of lattice vibrations. In Sec. III we discuss aspects of the Debye model of lattice vibrations that are relevant to spin-lattice relaxation in the high-temperature limit. In Sec. IV we demonstrate how the fluctuations described in the Debye model lead to the direct and Raman contributions to spin-lattice relaxation. In Secs. V and VI we apply the model to obtain expressions for relaxation due to the dipolar and spin-rotation interactions. In Sec. VII we estimate numerical values of relaxation times for several cases and demonstrate that the spin-rotation interaction is, indeed, a relaxation mechanism that yields relaxation rates with the observed order of magnitude. Finally, we present a summary in Sec. VIII.

II. SEMICLASSICAL FREQUENCY-MODE MODEL OF NUCLEAR SPIN-LATTICE RELAXATION

An ensemble of nuclear spins of gyromagnetic ratio γ interacts with a strong externally applied static magnetic field $\mathbf{B}_0$ in the z direction. We restrict the consideration to a system of mutually noninteracting spins 1/2. Random lattice motions produce a weak randomly fluctuating magnetic field $\Delta\mathbf{B}(t)$ at the site of each spin. The time average of $\Delta\mathbf{B}(t)$ is zero. The very general nuclear spin-lattice relaxation theory presented in this section does not include a model for the physical origins of $\Delta\mathbf{B}(t)$; that is done in the sections that follow. It is a semiclassical model in the sense that the nuclear spins are described quantum mechanically, while the lattice is described as a classical entity producing $\Delta\mathbf{B}(t)$. The nuclear spin Hamiltonian in the laboratory frame is

$$H(t) = \omega_0 I_z + \gamma\Delta B_x(t)I_x + \gamma\Delta B_y(t)I_y + \gamma\Delta B_z(t)I_z, \quad (2.1)$$

where $\omega_0 = \gamma B_0$ is the nuclear resonance frequency. It is assumed that the fluctuations of the x, y, and z components are uncorrelated. The autocorrelation functions $G(\tau)$ of $\gamma\Delta B_x(t)$ and $\gamma\Delta B_y(t)$ are

$$G(\tau) = \gamma^2\langle\Delta B_x(t)\Delta B_x(t+\tau)\rangle = \gamma^2\langle\Delta B_y(t)\Delta B_y(t+\tau)\rangle, \quad (2.2)$$

where $\langle\rangle$ indicates the average over an ensemble. The z component of $\Delta\mathbf{B}$ does not contribute to longitudinal relaxation. By virtue of the ergodic theorem, the ensemble average is identical to the average over t. As indicated in Eq. (2.2), ΔB_x and ΔB_y are assumed to have the same autocorrelation functions. The mean-square local field is given by

$$\langle\Delta B^2\rangle = \langle\Delta B_x^2\rangle + \langle\Delta B_y^2\rangle + \langle\Delta B_z^2\rangle = 3G(0)/\gamma^2. \quad (2.3)$$

The spectral density, $J(\omega)$, is defined as the Fourier transform of $G(\tau)$,

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau)\exp(-i\omega\tau)d\tau. \quad (2.4)$$

The nuclear spin-lattice relaxation rate $1/T_1$ is proportional to the spectral density at ω_0, the proportionality coefficient being equal to $1/2$ for spins $1/2$:[31–37]

$$\frac{1}{T_1} = \frac{1}{2}J(\omega_0). \quad (2.5)$$

One of two approaches can be chosen to derive an expression for $J(\omega_0)$ from characteristic properties of the lattice, the choice being dictated by the nature of the lattice-dynamics model. Traditionally, the best-known approach in nuclear spin-lattice relaxation theory is the correlation-time approach. It is briefly described below. The alternative approach is a frequency-mode model, which we present in the semiclassical form. The random local fields $\Delta B_x(t)$ and $\Delta B_y(t)$ in Eq. (2.1) are modeled as superpositions of very many oscillation modes,

$$\Delta B_q(t) = \sum_i b(\omega_i)\cos(\omega_i t + \phi_{q,i}), \quad (2.6)$$

with $q = x, y$. ΔB_x and ΔB_y have identical mode frequencies ω_i and amplitudes $b(\omega_i)$, but their phases $\phi_{x,i}$ and $\phi_{y,i}$ are uncorrelated. [Note that Eq. (2.6) cannot be viewed as a Fourier series because the frequencies are not necessarily regularly spaced.] The frequencies ω_i in the summation of Eq. (2.6) form a quasicontinuum from 0 to some yet-to-be-defined ω_{max}. Rather than defining the frequencies explicitly, they are specified by a density of modes, $\eta(\omega)$, in frequency space. Since the amplitude $b(\omega_i)$ of each mode is not necessarily uniform across the ensemble, its magnitude is specified by the mean-square amplitude $\langle b(\omega_i)^2\rangle$. A calculation of the square of ΔB_q by substitution of Eq. (2.6) in Eq. (2.3) yields two types of terms, i.e., squares of contributions of individual modes, $b(\omega_i)^2\cos^2(\omega_i t + \phi_{q,i})$, and cross-products of modes with different frequencies. Since the time averages of the cross-products vanish, the mean square of the total is the sum of the averages of the squares of the individual modes. In integral form the averages of the squares of the x and y components are given by

$$\langle \Delta B_x^2 \rangle = \langle \Delta B_y^2 \rangle = \int_0^{\omega_{max}} \eta(\omega) \langle b(\omega)^2 \cos^2(\omega t + \phi_\omega) \rangle d\omega$$

$$= \frac{1}{2} \int_0^{\omega_{max}} \eta(\omega) \langle b(\omega)^2 \rangle d\omega. \qquad (2.7)$$

The autocorrelation function, as defined in Eq. (2.2), is similarly reduced to

$$G(\tau) = \gamma^2 \int_0^{\omega_{max}} \eta(\omega) \langle b(\omega)^2 \cos(\omega t) \cos[\omega(t + \tau)] \rangle d\omega$$

$$= \frac{1}{2} \gamma^2 \int_0^{\omega_{max}} \eta(\omega) \langle b(\omega)^2 \rangle \cos(\omega \tau) d\omega. \qquad (2.8)$$

Its Fourier transform is the spectral density,

$$J(\omega) = \pi \gamma^2 \eta(\omega) \langle b(\omega)^2 \rangle. \qquad (2.9)$$

Hence, according to Eq. (2.5), the spin-lattice relaxation rate, is given by

$$\frac{1}{T_1} = \frac{\pi}{2} \gamma^2 \eta(\omega_0) \langle b(\omega_0)^2 \rangle. \qquad (2.10)$$

The semiclassical frequency-mode model of nuclear spin-lattice relaxation developed here differs from the more traditional correlation-time approach to nuclear spin-lattice relaxation. The latter begins with Eqs. (2.4) and (2.5) but then the correlation function in Eq. (2.4) is defined in terms of a correlation time τ_c with a common assumption being

$$G(\tau) = G(0) \exp(-|\tau|/\tau_c), \qquad (2.11)$$

where, according to Eq. (2.3), $(3/\gamma^2)G(0) = \langle \Delta B^2 \rangle$ is the total mean-square magnitude of the fluctuating field. It then follows from the discussion above that

$$\frac{1}{T_1} = \frac{1}{3} \gamma^2 \langle \Delta B^2 \rangle \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}. \qquad (2.12)$$

This formulates the dynamic process in the time domain by specification of (a) the correlation time and (b) the size of the entire fluctuating Hamiltonian (in this case $\gamma^2 \langle \Delta B^2 \rangle$, in the case of dipolar relaxation the second moment, etc.). By contrast, in a frequency-mode analysis used above, one describes the process in the frequency domain by specifying (a) the mean-square amplitude $\langle b(\omega)^2 \rangle$ of the frequency-mode amplitudes and (b) their mode density $\eta(\omega)$. From the point of view of information content, these are not equivalent starting points. Since $1/T_1$ depends on the behavior of the fluctuations in the frequency range around the NMR frequency, it is sufficient to specify $\langle b(\omega)^2 \rangle$ and $\eta(\omega)$ at $\omega = \omega_0$ only, as will be done in the following sections. In the correlation-time approach, on the other hand, the mean square magnitude $\langle \Delta B^2 \rangle$ of the local field and the correlation time τ_c combine information about the *entire spectrum* of fluctuations, from which the spectral density at the NMR frequency is to be extracted by Fourier transformation.

The correlation time is very often a useful parameter because it simplifies the characterization of a monotonically decaying correlation function. In fact, motional models such as chemical kinetics and rotational diffusion directly imply exponentially decaying correlation functions. Moreover, the total mean-square magnitude $\gamma^2 \langle \Delta B^2 \rangle$ of the fluctuating interaction is a readily defined parameter in many relaxation mechanisms. However, in the formalism of a frequency-mode analysis developed in this section, the correlation time is a rather meaningless concept for two reasons. First, the correlation function is dominated by modes in frequency regions that are entirely irrelevant to the relaxation mechanism and about which little or nothing may be known. Second, the correlation function may not be a smoothly decaying function of time. In fact, an application of Eq. (2.8) to the evaluation of the correlation function of the fluctuating magnetic fields generated by lattice vibrations (using mathematical models to be presented in Sec. III) shows that the correlation function of those fields is a strongly oscillating function of time. No further reference will therefore be made to a correlation time or, for similar reasons, to the total mean-square magnitude of the local field fluctuations.

The two semiclassical approaches described above have in common that they make use of the classical spectral density evaluated at the NMR frequency to evaluate the nuclear spin-lattice relaxation rate. In this, they *both* differ from the quantum-mechanical theory originally developed for spin-lattice relaxation due to lattice vibrations.[20–22] In that approach, the relaxation process is described as transitions among combination states of phonons and spins, with transition rates that are derived from time-dependent perturbation theory (Fermi's Golden Rule). Nevertheless, most elements of the physical description of the relaxation process introduced in the original theory are adopted without change in the semiclassical frequency-mode formalism further developed below. In our view it is a convenient and practical way to describe the random field fluctuations in a meaningful classical picture.

III. DEBYE MODEL OF LATTICE VIBRATIONS

As indicated, the lattice-vibration pathway of nuclear spin relaxation is best evaluated by determination of the mean-square amplitudes of the magnetic-field oscillations $\langle b(\omega)^2 \rangle$ and the density of modes $\eta(\omega)$ introduced in the previous section. Their values at ω_0 are the only two parameters needed in the expression for $1/T_1$ in Eq. (2.10). We now describe a model of atomic vibrational modes in a solid to which these two parameters can be related. Following the original theoretical formalism,[20–22] we adopt the Debye model of acoustical vibrations[38–40] to describe the lattice dynamics that cause relaxation. In that model, the fluctuating displacements $\mathbf{u}(t)$ of the atoms from their equilibrium positions $\mathbf{r}$ are described as the superposition of normal modes. In a normal mode, all atoms in the crystal vibrate in concert with the same frequency. In a multiatom lattice, one distinguishes between acoustical and optical modes. The acoustical modes are propagating harmonic waves with wavelengths that are longer than the interatomic distances. The summation over the acoustical modes can be written

$$\mathbf{u}(t) = \sum_i \boldsymbol{\xi}_i \cos(\omega_i t + \mathbf{k}_i \cdot \mathbf{r} + \phi_i), \qquad (3.1)$$

where $\boldsymbol{\xi}_i$, ω_i, $\mathbf{k}_i$, and ϕ_i are, respectively, the amplitude, the frequency, the wave vector, and the phase of mode i. In such

long-wavelength modes, neighboring atoms vibrate with the same amplitude and nearly in phase with each other, irrespective of their individual masses or their individual force constants. By contrast, the optical modes are dominated by relative motions of adjacent atoms. They resemble the vibrational modes of isolated molecules. Their frequencies are higher than those of the acoustical modes. Optical modes are generally not taken into account in nuclear spin-lattice relaxation theory.[20–22]

The Debye model[39,40] is based on several simplifying approximations, which may be summarized as follows: (i) There are no acoustical modes with frequencies ω above the Debye frequency ω_D, (ii) between $\omega=0$ and ω_D the density of modes in frequency space is proportional to ω^2, and (iii) the wavelengths $\lambda \equiv 2\pi/k$ and the frequencies ω of the modes are related by a dispersion relation that is characterized by a uniform sound velocity, v

$$v = \frac{\omega\lambda}{2\pi} = \frac{\omega}{k}. \qquad (3.2)$$

Since nuclear spin-lattice relaxation theory does not usually distinguish between the amplitudes and velocities of transverse and longitudinal modes,[22] the atomic vibrations in the acoustical modes are considered isotropic. The Debye frequency is related to the Debye temperature Θ_D by

$$k_B\Theta_D = \hbar\,\omega_D, \qquad (3.3)$$

where k_B is Boltzmann's constant. Typically, Θ_D of ionic crystals is between 150 and 350 K,[38] corresponding to $\omega_D/2\pi$ ranging from 3 to 7×10^{12} Hz. A typical sound velocity is 5×10^3 m/s. According to Eq. (3.2), this value corresponds to a wavelength between 7 and 17 Å at the Debye frequency. Since this is the shortest wavelength, acoustical wavelengths are longer than interatomic distances, as assumed in the model.

To complete the thermal description of the acoustical vibrations, the total number of modes and the vibrational amplitudes need to be modeled. The combined number of acoustical and optical modes is $3N$, where N is the number of atoms in the crystal. A monatomic crystal has no optical modes. The density of modes for a monatomic crystal is, therefore,

$$\sigma(\omega) = \frac{9N\omega^2}{\omega_D^3}, \qquad (3.4)$$

which gives $3N$ when integrated from 0 to ω_D. Multiatom lattices are briefly discussed below.

The amplitudes of the atomic vibrations follow a temperature-dependent statistical distribution. In the original theories of nuclear spin-lattice relaxation due to lattice vibrations, the relaxation mechanism is treated as consisting of elementary energy-conserving simultaneous transitions among phonon quantum states and nuclear spin states.[21,22] The thermal aspect of this process enters via the thermal populations of the phonon states, which are governed by Bose-Einstein statistics. In such theories, an expression for vibrational amplitudes is not needed and is consequently not given in the treatments presented in the literature. However,

in the semiclassical approach presented here, explicit knowledge of the amplitudes is essential. To this end, classical statistical mechanics provides values for the amplitudes, which are readily applicable to our situation in the high-temperature limit ($T > \Theta_D$). We recall that the total energy of a harmonic oscillator of mass M, frequency ω, and amplitude ξ is the sum of the kinetic and potential energies, K and P and is given by

$$E = K + P = \frac{1}{2}M\xi^2\omega^2. \qquad (3.5)$$

The energy of a vibrational mode is the sum of the energies of the N atoms participating in it. Its energy is thus given by Eq. (3.5) with M replaced by Nm, where m is the average mass of the atoms in the crystal. By equipartition, the average energy at high temperature is equal to k_BT. The thermal average of the square of the vibrational amplitude ξ of the mode is therefore

$$\langle\xi(\omega)^2\rangle = \frac{2k_BT}{Nm\omega^2}. \qquad (3.6)$$

This result can be used to calculate the mean-square displacement $\langle u^2\rangle$ of atoms from their equilibrium positions. Following the same argument that led to Eq. (2.7) and realizing that the density of modes includes vibrations in all three dimensions, one obtains

$$\langle u^2\rangle = \langle u_x^2\rangle + \langle u_y^2\rangle + \langle u_z^2\rangle = \frac{1}{2}\int_0^{\omega_D}\sigma(\omega)\langle\xi(\omega)^2\rangle d\omega = \frac{9k_BT}{m\omega_D^2}. \qquad (3.7)$$

In crystallography, the thermal displacements of atoms in a crystal are of interest because the random displacements reduce the certainty with which the atomic positions can be known and thus cause a reduction of the diffraction intensities. These effects are quantified in the form of the Debye-Waller factors, which are functions of the mean-square displacement $\langle u^2\rangle$ of the atoms. Crystallographers derive the result given in Eq. (3.7) in the high-temperature approximation.[40]

In multiatomic crystals with identifiable molecular units having strong internal chemical bonds, such as a molecule in a molecular crystal or the NO_3^- ion in a nitrate, one distinguishes between "internal" vibrational modes of the molecular units and "external" modes that involve translations and rotations of rigid ions.[38,40] The internal (optical) modes are high-frequency vibrations such as those in gas molecules. However, the external modes contain, in addition to Debye-type acoustical modes, other vibrations with frequencies in the acoustical range and with dispersion relations that deviate strongly from the simple k-to-ω proportionality of Eq. (3.2).[38] Although the dispersion maps of many ionic crystals, including $Pb(NO_3)_2$,[41,42] are accurately known and often well understood in terms of interatomic forces,[38] the complexity of the model developed here does not allow us to incorporate them fully in a generalized nuclear spin-lattice relaxation theory. Therefore, we continue with a theoretical description of the crystal vibrations according to the Debye model, using
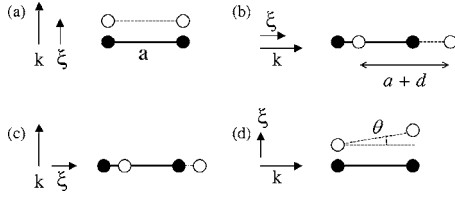
FIG. 1. Relative positions of two neighboring atoms participating in an acoustical lattice vibration mode. Closed and open circles are atoms in equilibrium and displaced positions, respectively. Four cases of relative orientations of the propagation vector **k**, the displacement vector $\boldsymbol{\xi}$, and the interatomic vector **a** are illustrated. Left and right columns: Planar wave propagation perpendicular and parallel to **a**, respectively. Top and bottom rows: Longitudinal and transverse modes, respectively.

experimentally determined sound velocities and Debye temperatures to make quantitative predictions.

To determine relaxation effects, one must specify how vibrations in the Debye model affect the magnetic-field oscillation modes. Nuclear spin interactions generally depend on relative distances and/or orientations of interatomic vectors from one spin to another. For instance, dipolar interactions depend on internuclear distances and on orientations of internuclear vectors with respect to the magnetic field; chemical shifts are functions of the internal geometry of molecules; anisotropic effects are caused by reorientations of atomic clusters; and the spin-rotation interaction is due to the rotations of molecules. A simultaneous translation of a nucleus and its environment does not have an effect on these interactions. In other words, the spin Hamiltonian is a function of local strain rather than of atomic displacement per se. Therefore, one must begin with a mode analysis of atomic distances and of orientations of interatomic vectors.

Consider the relative motions of two adjacent atoms, separated by an equilibrium-position vector **a** of length a and participating in an acoustical mode of frequency ω, amplitude $\boldsymbol{\xi}$, and wave vector **k**. The wave propagation is in the direction of **k**. Taking into account that **a**, $\boldsymbol{\xi}$, and **k** are vector quantities, we distinguish nine possible relative orientations of $\boldsymbol{\xi}$ and **k** along orthogonal directions with respect to a given **a**, four examples of which are depicted in Fig. 1. When **k** is perpendicular to **a**, such as in the longitudinal wave shown in Fig. 1(a) and in the transverse wave shown in Fig. 1(c), the wave propagation is such that the two atoms under consideration vibrate in phase and neither the distance nor the relative orientation of the two atoms is modulated. Hence, only three of the nine vibrational modes, those that have **k**//**a**, can be active as spin relaxation agents. Of those, we distinguish between one longitudinal ($\boldsymbol{\xi}$//**k**) mode as shown in Fig. 1(b) and two transverse ($\boldsymbol{\xi}\perp$**k**) modes, as shown in Fig. 1(d).

In the remainder of this section, we present expressions for the mean amplitudes and mode densities of the lattice parameters that are relevant to the relaxation theory. The notation used to describe these parameters is summarized in Table II. We begin with the distance fluctuations. The longitudinal modes of the type represented in Fig. 1(b) modulate the interatomic distance $a+d(t)$, with $d(t)$ given by

TABLE II. Notation for fluctuating geometric and magnetic parameters.

Parameter	Equilibrium value	Deviation from equilibrium	Mode amplitude
Atom position	**r**	**u**	$\boldsymbol{\xi}$
Interatomic distance	a	d	δ
Orientation of interatomic vector	–	θ	χ
Angular velocity of interatomic vector	0	Ω	ψ
Local magnetic field	B_{loc}	ΔB	b

$$d(t) = \sum_{i \in b} \xi_i \{\cos(\omega_i t + k_i a + \phi_i) - \cos(\omega_i t + \phi_i)\}, \quad (3.8)$$

where the notation $i \in b$ indicates that the sum over the vibrational modes is restricted to those that satisfy the condition of Fig. 1(b), $\boldsymbol{\xi}_i$//**k**$_i$//**a**. For $k_i a \ll 1$, the expression in braces in Eq. (3.8) reduces to $-k_i a \sin(\omega_i t + \phi_i)$, while for $k_i a = \pi$ (for the highest possible acoustical wave number), it is $-2 \cos(\omega_i t + \phi_i) = -(2/\pi)ka \cos(\omega_i t + \phi_i)$. As such, we approximate Eq. (3.8) as

$$d(t) = \sum_{i \in b} \xi_i(\omega_i) k_i a \cos(\omega_i t + \phi_i') = \sum_{i \in b} \delta_i(\omega_i) \cos(\omega_i t + \phi_i'),$$

$$(3.9)$$

where ϕ_i' is ϕ_i plus a k_i-dependent phase correction. In Eq. (3.9) we introduce an oscillation amplitude $\delta_i(\omega_i)$ for the distance fluctuation, which, after substitution of the Debye dispersion relation, $k_i = \omega_i/v$, can be seen to be equal to $\xi_i(\omega_i)a\omega_i/v$. Using Eq. (3.6), we find that the distance-oscillation modes of frequency ω have a mean-square amplitude

$$\langle \delta(\omega)^2 \rangle = \frac{2k_B T a^2}{N m v^2}. \quad (3.10)$$

Since only one out of nine vibrational modes contributes to the distance modulation, the effective density of modes is $\sigma(\omega)/9$, with $\sigma(\omega)$ as given in Eq. (3.4).

Next we consider the modulation θ of the angles in Fig. 1(d). The transverse modes depicted in Fig. 1(d) do not modulate the distance to first order, but they cause the vector connecting the two atoms to change direction over a small angle

$$\theta(t) = \sum_{i \in d} \{\xi_i(\omega_i)/a\}\{\cos(\omega_i t + k_i a + \phi_i) - \cos(\omega_i t + \phi_i)\},$$

$$(3.11)$$

where the summation is restricted to modes satisfying the condition $\boldsymbol{\xi}_i \perp$ **k**$_i$//**a**. By reasoning analogous to that for longitudinal modes, this can be written as a sum of angular oscillations

$$\theta(t) = \sum_{i \in d} \chi_i(\omega_i)\cos(\omega_i t + \phi_i'), \quad (3.12)$$

with angular amplitudes $\chi_i(\omega_i) = k_i a \xi_i(\omega_i)/a = \xi_i(\omega_i)\omega_i/v$. Their mean-square amplitude is

$$\langle \chi(\omega)^2 \rangle = \frac{2k_B T}{Nmv^2}, \quad (3.13)$$

and the effective density of these modes is $2\sigma(\omega)/9$.

Finally, to an angular oscillation $\theta(t)$ corresponds an angular velocity $\Omega(t) = d\theta/dt$. Hence, each angular oscillation mode of amplitude $\chi_i(\omega_i)$ can also be described as an angular-velocity mode that oscillates with an amplitude $\psi_i(\omega_i) = \omega_i \chi_i(\omega_i)$, as can be seen from

$$\Omega(t) = d\theta/dt = -\sum_{i \in d} \omega_i \chi_i(\omega_i)\sin(\omega_i t + \phi_i')$$

$$= \sum_{i \in d} \psi_i(\omega_i)\sin(\omega_i t + \phi_i'). \quad (3.14)$$

The mean-square angular-velocity amplitude is

$$\langle \psi(\omega)^2 \rangle = \frac{2k_B T \omega^2}{Nmv^2}. \quad (3.15)$$

and the density of modes is $2\sigma(\omega)/9$.

IV. DIRECT AND RAMAN RELAXATION PROCESSES

In this section the relationship between the lattice-vibration modes and the local magnetic oscillation modes is established, and general expressions for the nuclear spin-lattice relaxation rates are derived. The derivation is first carried out in detail for a nuclear spin interaction that is modulated by atomic distance fluctuations $d(t)$ only. The theory is subsequently extended to include interactions that also depend on orientation fluctuations $\theta(t)$ and angular-velocity fluctuations $\Omega(t)$.

Let the local magnetic field $\mathbf{B}_{\text{loc}}$ at the site of the nuclear spin be a function of an interatomic distance. When the distance changes from a to $a+d$, the local field becomes $\mathbf{B}_{\text{loc}} + \Delta\mathbf{B}(d)$. For small displacements we write the x component of the field modulation as a second-order power series in d,

$$\Delta B_x = f_1 d + f_2 d^2. \quad (4.1)$$

Specific examples of the parameters f_1 and f_2 and of other similar parameters to be introduced below are discussed and modeled in Sec. V. It was first recognized by Waller in 1932 in his theory of paramagnetic relaxation by electron-spin dipolar interactions,[20] and later corroborated by Heitler and Teller in their theory of paramagnetic relaxation due to fluctuations of the ligand field,[23,43] as well as by van Kranendonk in his theory of nuclear spin-lattice relaxation by quadrupolar interactions,[21] that linear and quadratic terms of a spin interaction as a function of lattice strain generate two separate relaxation pathways, known as the direct process and the Raman process, respectively. Here we restate the theory in terms of a semiclassical model of fluctuating magnetic fields as described in Sec. II. Treating $d(t)$ as a sum of distinct

vibration modes, substitution of Eq. (3.9) in Eq. (4.1) gives

$$\Delta B_x(t) = f_1 \sum_i \delta(\omega_i)\cos(\omega_i t)$$

$$+ f_2 \sum_{i,j} \delta(\omega_i)\delta(\omega_j)\cos(\omega_i t)\cos(\omega_j t). \quad (4.2)$$

For conciseness of notation, the random phases ϕ_i and ϕ_j in Eq. (3.9) are omitted. Converting the products of cosines in the second term to combinations of oscillations at sum and different frequencies gives

$$\Delta B_x(t) = f_1 \sum_i \delta(\omega_i)\cos(\omega_i t) + \frac{1}{2}f_2 \sum_{i,j} \delta(\omega_i)\delta(\omega_j)$$

$$\times \{\cos[(\omega_i - \omega_j)t] + \cos[(\omega_i + \omega_j)t]\}. \quad (4.3)$$

$\Delta B_x(t)$ and, by analogy $\Delta B_y(t)$, are, by Eq. (4.3), in a form that resembles the starting point of the frequency-domain nuclear spin-lattice relaxation model introduced in Sec. II. To make the connection, one must find the relationship between the mean-square amplitudes of the local fields $\langle b(\omega)^2 \rangle$ [introduced in Eq. (2.6)] and the density of modes $\eta(\omega)$ [introduced in Eq. (2.7)] of the magnetic fluctuations on the one hand, and the corresponding vibrational quantities $\langle \delta(\omega)^2 \rangle$ and $\sigma(\omega)$ [Eqs. (3.10) and (3.4)] on the other hand. As pointed out in Sec. II, nuclear spin-lattice relaxation is driven by terms that oscillate at the NMR frequency ω_0. In the summation of the (linear) f_1 term, only the cosine terms oscillating at ω_0 contribute to nuclear spin relaxation. The linear term, therefore, represents a process whereby phonons in resonance with the NMR frequency exchange energy quanta directly with the spins. In the summation of the (quadratic) f_2 term, any harmonic vibration pair satisfying the relation $|\omega_i \pm \omega_j| = \omega_0$ enables relaxation. In this relationship, the minus sign represents a Raman-type scattering process where one phonon at ω_i is annihilated and another one at ω_j is created, or vice versa, with the energy difference being supplied by a flipping nuclear spin. The plus sign represents simultaneous creation (or annihilation) of two phonons, the sum of whose energies match that of a spin flip.

By comparing Eq. (2.6) with Eq. (4.2), it can be seen that the oscillating magnetic field generated by the linear f_1 term at the NMR frequency has an amplitude $b(\omega_0) = f_1 \delta(\omega_0)$. Its density of modes $\eta(\omega_0)$ is the same as that of the vibrational modes that modulate interatomic distances, i.e., $\sigma(\omega_0)/9$. Combining this with Eqs. (2.10), (3.4), and (3.10) yields the relaxation rate of the direct process,

$$\frac{1}{T_{1\text{direct}}} = \frac{\pi\gamma^2 f_1^2 a^2 k_B T \omega_0^2}{mv^2 \omega_D^3}. \quad (4.4)$$

In the double-summation f_2 term of Eq. (4.3), every (ω_i, ω_j) combination whose sum or difference equals ω_0 contributes to spin-lattice relaxation. The locus of these frequency pairs in the two-dimensional frequency space (ω_1, ω_2) is indicated in Fig. 2. Since the phases of these distinct oscillating terms are not correlated, the combined nuclear spin-lattice relaxation rate is the sum of the individual relaxation rates. Each (ω_1, ω_2) pair generates an oscil-
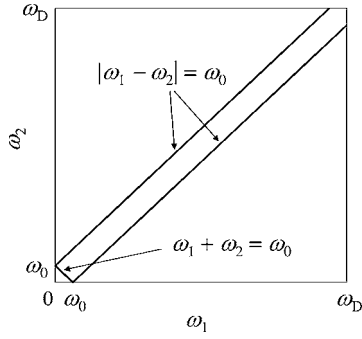
FIG. 2. Two-dimensional frequency space showing the locus of points whose sum or difference equals the NMR frequency. These lines represent the trajectory of integration for evaluation of the Raman contributions to relaxation. Because $\omega_0 \ll \omega_D$, the contribution of the sum section is negligible, while the difference sections nearly collapse to two lines coinciding with the diagonal.

lating field of amplitude $b(\omega_1, \omega_2) = f_2 \delta(\omega_1) \delta(\omega_2)/2$ [see Eq. (4.3)] and has a two-dimensional mode density given by $\eta(\omega_1, \omega_2) = \sigma(\omega_1)\sigma(\omega_2)/81$. Its mean-square amplitude is $\langle b(\omega_1, \omega_2)^2 \rangle = f_2^2 \langle \delta(\omega_1)^2 \delta(\omega_2)^2 \rangle/4$, which can be written as $f_2^2 \langle \delta(\omega_1)^2 \rangle \langle \delta(\omega_2)^2 \rangle/4$ because the phases of the vibrational modes at ω_1 and ω_2 are uncorrelated. The relaxation rate is the sum of the $1/T_1$ contributions from all (ω_1, ω_2) pairs having their difference or sum equal to ω_0. Thus, the total Raman relaxation rate is the line integral of

$$\frac{\pi}{648} \gamma^2 \sigma(\omega_1)\sigma(\omega_2) f_2^2 \langle \delta(\omega_1)^2 \rangle \langle \delta(\omega_2)^2 \rangle \quad (4.5)$$

over the trajectory in Fig. 2. Since the NMR frequency ω_0 is typically five orders of magnitude smaller than the Debye frequency ω_D, the integral may be approximated as

$$\frac{1}{T_{1\text{Raman}}} = 2\sqrt{2} \int_0^{\omega_D} \frac{\pi}{648} \gamma^2 \sigma(\omega)^2 f_2^2 \langle \delta(\omega)^2 \rangle^2 d\omega. \quad (4.6)$$

Substitution of Eqs. (3.10) and (3.4) for $\langle \delta(\omega)^2 \rangle$ and $\sigma(\omega)$, respectively, gives for the Raman process

$$\frac{1}{T_{1\text{Raman}}} = \frac{2\pi\sqrt{2}\gamma^2 f_2^2 a^4 k_B^2 T^2}{5m^2 v^4 \omega_D}. \quad (4.7)$$

These results display the following well-known properties of the direct and Raman processes.[20–22] $1/T_{1\text{direct}}$ is proportional to the temperature T and to the square of the NMR frequency ω_0, whereas $1/T_{1\text{Raman}}$ is proportional to the square of the temperature T and is independent of ω_0. The ω_0 dependence will be different if the coefficients f_1 and f_2 are themselves functions of ω_0, a situation that is encountered when the magnetic coupling arises from a fluctuating chemical shift. Furthermore, the Raman process is much more efficient than the direct process, as is evident from the ratio of the two ($1/T_1$)'s,

$$\frac{T_{1\text{direct}}}{T_{1\text{Raman}}} = \frac{2\sqrt{2}a^2 f_2^2}{5f_1^2} \frac{k_B T}{mv^2} \frac{\omega_D^2}{\omega_0^2}. \quad (4.8)$$

It is commonly found that af_2 and f_1 are of comparable order of magnitude.[20–22] From the sizes of the other two factors in this expression, $k_B T/mv^2 \gtrsim 0.001$ and $(\omega_D/\omega_0)^2 \sim 10^{10}$, it is seen that $1/T_{1\text{direct}}$ is many orders of magnitude smaller than $1/T_{1\text{Raman}}$.

This shows that the second-order term in the power expansion of ΔB_x as a function of d generates a far more efficient relaxation pathway than does the first-order term. Does this imply that a third-order term is even more effective? To investigate this, one can apply the same analysis as outlined above to an $f_3 d^3$ term in the expansion of ΔB_x in Eq. (4.1). The expression for the relaxation rate then involves double integrals of

$$f_3^2 \sigma(\omega_1)\sigma(\omega_2)\sigma(\omega_3)\langle \delta(\omega_1)^2 \rangle \langle \delta(\omega_2)^2 \rangle \langle \delta(\omega_3)^2 \rangle \quad (4.9)$$

over planar cross sections of the three-dimensional frequency space. This integration yields a contribution to the relaxation rate of the order of

$$\frac{1}{T_{1(3)}} \approx \frac{f_3^2 a^6 k_B^3 T^3}{m^3 v^6 \omega_D}, \quad (4.10)$$

having a T^3 dependence on the temperature. The ratio of the relaxation rates $1/T_{1\text{Raman}}$ and $1/T_{1(3)}$ is given by

$$\frac{T_{1(3)}}{T_{1\text{Raman}}} \approx \frac{f_2^2}{a^2 f_3^2} \frac{mv^2}{k_B T}. \quad (4.11)$$

If f_2 and af_3 are of comparable sizes, the Raman relaxation is two or three orders of magnitude more effective than relaxation originating in the third-order term. Thus, unless af_3 is very much larger than f_2, one is justified in terminating the power series of ΔB_x after the second term.[21,22] In actual experimental situations, this condition will be verified by the observed T^2 dependence of the relaxation rate.

Next we consider the situation where the local magnetic field depends on the angle θ between a strained interatomic vector and its orientation in the rest position,

$$\Delta B_x = g_1 \theta + g_2 \theta^2. \quad (4.12)$$

Nuclear spin-lattice relaxation in this case is caused by the creation/annihilation of transverse-mode phonons of the type illustrated in Fig. 1(d). Derivations similar to those of Eqs. (4.4) and (4.7) give

$$\frac{1}{T_{1\text{direct}}} = \frac{2\pi\gamma^2 g_1^2 k_B T \omega_0^2}{mv^2 \omega_D^3}, \quad (4.13)$$

$$\frac{1}{T_{1\text{Raman}}} = \frac{8\pi\sqrt{2}\gamma^2 g_2^2 k_B^2 T^2}{5m^2 v^4 \omega_D}. \quad (4.14)$$

Another possible relaxation process is one enabled by a second-order term proportional to the product of distance and orientation strains,

$$\Delta B_x = h_2 \theta d. \qquad (4.15)$$

The corresponding Raman relaxation rate, caused by the simultaneous creation and annihilation of longitudinal and transverse phonons, is similarly given by

$$\frac{1}{T_{1\mathrm{Raman}}} = \frac{4\pi\sqrt{2}\,\gamma^2 a^2 h_2^2 k_B^2 T^2}{5 m^2 v^4 \omega_D}. \qquad (4.16)$$

Of special relevance to the spin-lattice relaxation of heavy nuclei in ionic crystals is the case of the spin-rotation interaction. It is driven by angular-velocity fluctuations Ω to first and second order and by cross-products with the other displacement parameters,

$$\Delta B_x = i_1 \Omega + i_2 \Omega^2 + j_2 \Omega d + k_2 \Omega \theta. \qquad (4.17)$$

For reasons discussed below, we will only be concerned with the direct process due to the i_1 term and the Raman process due to the j_2 term. With these restrictions, the direct process involves transverse vibration modes, while the Raman process is due to simultaneous longitudinal and transverse modes. The rates of these relaxation processes are given by

$$\frac{1}{T_{1\mathrm{direct}}} = \frac{2\pi\gamma^2 i_1^2 k_B T \omega_0^4}{m v^2 \omega_D^3} \qquad (4.18)$$

and

$$\frac{1}{T_{1\mathrm{Raman}}} = \frac{2\pi\sqrt{2}\,\gamma^2 a^2 j_2^2 \omega_D k_B^2 T^2}{7 m^2 v^4}. \qquad (4.19)$$

In the following two sections, these general equations are applied to direct and Raman nuclear spin-lattice relaxation due to the modulation of the dipolar interaction and the modulation of the spin-rotation interaction.

As already alluded to above, the actual density of modes and the dispersion relation between frequency and wavelength deviate considerably from the Debye model, even for the simplest crystal structures.[38–40] Fortunately these deviations do not have a severe impact on the principal features of the formulas for $1/T_{1\mathrm{direct}}$ and $1/T_{1\mathrm{Raman}}$ developed here. In the case of the Raman process, one notes that the formulas are derived from an integral over all vibration modes. Any deviation of $\sigma(\omega)$ or v from the Debye model is absorbed in the integral, with the result that the $1/T_1 = AT^2$ dependence is preserved as long as the temperature is high enough to validate the law of equipartition. This is undoubtedly the reason that the independence from ω_0 and the proportionality to T^2 of many of the relaxation rates listed in Table I are common features characteristic of the Raman process, regardless of the details of the vibrational model. On the other hand, for a quantitative estimate of the coefficient A of the T^2 dependence, there is generally no other choice than to invoke the Debye model. For the direct process, the question is somewhat academic in view of its small contribution to the relaxation. Nevertheless, we can make the observation that, although it depends explicitly on the vibrational properties at the NMR frequency, the $1/T_1 \propto T\omega_0^2$ and $1/T_1 \propto T\omega_0^4$ dependencies of Eqs. (4.13) and (4.18), respectively, probably remain valid because the Debye model is thought to be accurate for the low-frequency modes.[39]

Another simplification is that the interaction with only one single neighbor in the crystal lattice is taken into account. This is obviously quite unrealistic, as heavy metal ions can have as many as twelve neighboring oxygens in the crystal structure. Including all neighbors in the model is expected to enhance the theoretical relaxation rate by a substantial factor unless the coefficients f_2, g_2, etc., are defined such that they reflect the combined lattice strain of the total local environment. An explicit treatment of the many kinds of possible coordination environments is beyond the scope of the theory developed here.

V. DIPOLAR RELAXATION

To this point, the theory links the local time-dependent magnetic fields that are responsible for the nuclear spin-lattice relaxation to the time-dependent geometric parameters d, θ, and Ω. See Table II and Eqs. (4.1), (4.12), and (4.17) above and Eq. (5.2) below. Direct relaxation processes are driven by magnetic-field fluctuations that are linearly dependent on these parameters, whereas the field fluctuations responsible for Raman processes are either bilinear in these parameters or involve products of them. In the following section, we investigate the Raman process involving the product Ωd of angular velocity fluctuations and atomic distance fluctuations, which we identify with the spin-rotation mechanism responsible for nuclear spin-lattice relaxation in the compounds discussed previously and for which Eq. (1.1) is found. But first we consider direct and Raman dipolar relaxation, which is associated with terms involving only d and θ. The reason for doing so is that we are then able to check our model against the well-established model for dipolar relaxation as developed by Waller[20] and Abragam.[22] Chemical-shift relaxation is another example of a nuclear spin-lattice relaxation process driven by fluctuations of d (chemical-shift modulations due to a dependence on atomic distances) and θ (for instance, local field modulations due to rotations of the chemical-shift-anisotropy tensor). Since the local fields due to the chemical-shift interaction are proportional to ω_0, the resulting Raman relaxation rate is proportional to ω_0^2. In high-static fields, this mechanism could possibly begin to compete with spin-rotation relaxation.[6] In this paper, however, we do not apply our basic theory to the case of chemical-shift relaxation.

Consider a nuclear spin of gyromagnetic ratio γ_1 whose spin-lattice relaxation is caused by the fluctuating dipole field generated by a neighboring spin having a gyromagnetic ratio γ_2. Admittedly, this is a simplified description of the dipolar interaction between two spins. An adequate theory should be treated quantum mechanically with a two-spin Hamiltonian. However, in order to be able to apply the nuclear spin-lattice-relaxation theory of Sec. II, which was developed for isolated spins experiencing fluctuating fields, we follow this simplified approach. The internuclear distance is a and the polar angles of the internuclear vector with respect to a laboratory frame, whose z axis points along the magnetic field, are χ and ψ. If the second spin is quantized parallel to z, then the transverse components of the local field at the site of the first spin are given by

$$B_{\text{loc},x} = \frac{3\,\hbar\,\gamma_2 \sin 2\chi \cos \psi}{4a^3}; \quad B_{\text{loc},y} = \frac{3\,\hbar\,\gamma_2 \sin 2\chi \sin \psi}{4a^3}.$$
(5.1)

A distance deviation d and an orientation deviation θ modulate the local field in the x direction by an amount ΔB_x, which can be written as a power series in d and θ as follows:

$$\Delta B_x = f_1 d + g_1 \theta + f_2 d^2 + h_2 \theta d + g_2 \theta^2.$$
(5.2)

The coefficients f_1, g_1, etc., are functions of a, χ, and ψ and of the direction of the reorientation over θ. They are found by taking the appropriate derivatives of Eq. (5.1). Their magnitudes can be shown to be of the order

$$|f_1| \approx \hbar\,\gamma_2/a^4; \quad |g_1| \approx \hbar\,\gamma_2/a^3;$$

$$|f_2| \approx 2\,\hbar\,\gamma_2/a^5; \quad |h_2| \approx 2\,\hbar\,\gamma_2/a^4; \quad |g_2| \approx \hbar\,\gamma_2/a^3.$$
(5.3)

In the evaluation of the direct relaxation rate [Eqs. (4.4) and (4.13)], the contributions of the distance- and angle-modulating modes, quantified by f_1 and g_1, respectively, turn out to have the same parametric dependence on the relevant parameters. This allows them to be combined in the following single formula for the direct process due to the dipolar interaction with one neighboring nuclear spin:

$$\frac{1}{T_{1\text{direct}}^{\text{dip}}} \approx \frac{16\hbar^2 \gamma_1^2 \gamma_2^2 k_B T \omega_0^2}{mv^2 a^6 \omega_D^3}.$$
(5.4)

The Raman process [sum of Eqs. (4.7, 12, 16)] similarly gives

$$\frac{1}{T_{1\text{Raman}}^{\text{dip}}} \approx \frac{40\hbar^2 \gamma_1^2 \gamma_2^2 k_B^2 T^2}{m^2 v^4 a^6 \omega_D}.$$
(5.5)

Within a numerical factor of order unity, these formulas are equivalent to those derived by Abragam with the full quantum-mechanical theory.[22] The numerical discrepancy arises from the slightly different methods used to approximate coefficients such as f_1 and f_2 and from different implementations of the stretching and bending modes.

VI. SPIN-ROTATION RELAXATION

Atomic motion can induce an angular momentum in the electron distribution of an ion in a crystal and, consequently, can generate a magnetic field at the site of the nucleus, provided the atomic motion itself has an angular component with respect to the nucleus of the ion. On the other hand, the displacement of a neighboring atom that merely modulates the length of the interatomic vector and does not otherwise affect the environment, is ineffective as a source of magnetic field fluctuations in a spin-rotation interaction. Among the various kinds of diatomic vibrations shown in Fig. 1, only the one shown in Fig. 1(d) is magnetically active in this sense. It is characterized by an oscillating angular velocity Ω. Two of the nine possible orthogonal orientations of **k** and $\boldsymbol{\xi}$ with respect to **a** have that property.

We can use known values of spin-rotation constants in gas molecules to serve as a guide for estimating the typical size of a vibration-induced fluctuating magnetic field. The spin Hamiltonian for the spin-rotation interaction is usually written in the form[44,45]

$$H_{\text{SR}} = \mathbf{I} \cdot \mathbf{C} \cdot \mathbf{J}$$
(6.1)

for a nuclear spin operator **I**, a molecular angular momentum operator **J**, and a spin-rotation coupling tensor **C**. One normally thinks of it as the interaction of a nuclear magnetic moment operator $\boldsymbol{\mu}$ with a spin-rotation induced local magnetic field $\Delta \mathbf{B}_{\text{SR}}$,

$$H_{\text{SR}} = -\boldsymbol{\mu} \cdot \Delta \mathbf{B}_{\text{SR}} = -(\gamma \mathbf{I}) \cdot (\mathbf{C} \cdot \mathbf{J}/\gamma).$$
(6.2)

Indeed, for isolated molecules (dilute gases) Eq. (6.1) is a reasonable approach since **J** is a well-defined quantized constant of motion between collisions. Many values for **C** (or at least representative isotropic values C) are known from molecular spectroscopy. Fluctuations of **J** due to molecular collisions are a source of nuclear spin-lattice relaxation in gases.[46,47]

In the case of crystal lattice vibrations, Eq. (6.1) is not a useful form of the Hamiltonian because the concept of an angular momentum **J** requires the identification of an isolated structural unit that undergoes rotational motion as a rigid body, at least in first approximation. Such a structural unit is difficult to define unambiguously in a solid where the atoms perform simultaneous rotations with multiple neighboring partners in an endless array of interconnected structural subunits. Nevertheless, any time-dependent orientational position of one atom or ion with respect to another does distort the local electronic wave functions and, hence, produces a spin-rotation magnetic field $\Delta \mathbf{B}_{\text{SR}}$ at the site of a nucleus. One can argue that the primary physical quantity that determines the extent of this electronic distortion is the angular *velocity* of the electronically interacting atom pair rather than its angular *momentum*, which is the angular velocity multiplied by a moment of inertia. As such, we rewrite the Hamiltonian in Eqs. (6.1) and (6.2) as

$$H_{\text{SR}} = -(\gamma \mathbf{I}) \cdot (\boldsymbol{\Gamma} \cdot \boldsymbol{\Omega}),$$
(6.3)

whereby we introduce a tensor $\boldsymbol{\Gamma}$, which relates the induced magnetic field $\Delta \mathbf{B}_{\text{SR}}$ to the angular velocity $\boldsymbol{\Omega}$ of a small structural unit,

$$\Delta \mathbf{B}_{\text{SR}} = \boldsymbol{\Gamma} \cdot \boldsymbol{\Omega}.$$
(6.4)

This new tensorial coefficient can be applied to more general cases where angular velocities play a role but where moments of inertia are not necessarily well defined.

For freely rotating molecules, $\boldsymbol{\Gamma}$ can be derived from **C** by equating the quantum-mechanical and classical expressions that characterize the angular momentum, $\hbar J = I_m \Omega$, where I_m is the moment of inertia. (For simplicity, we do this analysis for the scalar equivalents of the vector/tensor quantities.) This leads to an expression for the local magnetic field in terms of the angular velocity

$$\Delta B_{\text{SR}} = -\frac{CJ}{\gamma} = -\frac{CI_m}{\hbar\gamma}\Omega,$$
(6.5)

and, hence, to

TABLE III. Spin-rotation parameters of several diatomic and tetrahedral molecules, where C=spin-rotation constant, I_m=molecular moment of inertia, γ=gyromagnetic ratio, Γ=magnetorotation constant.

Nucleus	Molecule	C (kHz)	I_m (10^{-45} kg m^2)	γ (10^7 T^{-1} s^{-1})	Γ (10^{-14} T s)	Reference
^{1}H	H$_2$	118.18	0.0046	26.750	−0.012	48
^{1}H	CH$_4$	10.50	0.053	26.752	−0.013	49
^{1}H	SiH$_4$	3.30	0.098	26.750	−0.007	49
^{1}H	GeH$_4$	4.00	0.104	26.750	−0.009	49
^{13}C	CH$_4$	15.94	0.053	6.728	−0.076	46
^{17}O	O$_2$	22.01	0.20	−3.628	0.73	50
^{19}F	LaF	35.60	1.14	25.166	−0.97	51
^{19}F	CF$_4$	−6.90	1.46	25.166	0.24	49
^{19}F	SiF$_4$	−2.42	2.00	25.166	0.12	49
^{19}F	GeF$_4$	−1.88	2.35	25.166	0.10	49
^{35}Cl	LaCl	2.71	2.92	2.621	−1.8	51
^{63}Cu	CuF	34.60	2.58	7.112	−7.5	52
^{81}Br	LaBr	7.41	6.02	7.224	−3.7	51
^{119}Sn	SnH$_4$	363.00	0.13	−9.998	2.8	30
^{119}Sn	SnD$_4$	183.00	0.26	−9.998	2.8	30
^{119}Sn	SnCl$_4$	6.00	8.23	−9.998	−3.0	30
^{121}Sb	Sb^{14}N	119.80	0.71	6.402	−7.9	53
^{121}Sb	Sb^{15}N	113.60	0.75	6.402	−8.0	53
^{121}Sb	SbF	87.60	1.01	6.402	−8.3	54
^{121}Sb	SbP	46.80	2.01	6.402	−8.8	53
^{121}Sb	SbCl	32.70	2.48	6.402	−7.6	54
^{127}I	LaI	5.79	9.20	5.352	−6.0	51
^{129}Xe	Xe$_2$	0.03	19.58	−7.452	0.048	6 and 55
^{139}La	LaF	9.35	1.14	3.779	−1.7	51
^{139}La	LaCl	13.01	2.92	3.779	−6.0	51
^{139}La	LaBr	8.69	6.02	3.779	−8.3	51
^{139}La	LaI	9.53	9.20	3.779	−13.9	51
^{175}Lu	LuF	8.76	1.05	3.055	−1.8	56
^{187}Os	OsO$_4$	−21.69	2.09	2.107	12.9	57
^{195}Pt	PtO	−54.07	0.74	5.838	4.1	58
^{195}Pt	PtS	66.80	1.66	5.838	−11.4	59
^{205}Tl	TlCl	73.00	3.25	15.692	−9.0	60
^{207}Pb	PbCl$_4$	2.9/7.8	9.28	5.550	−2.9/−7.8	29
^{207}Pb	Pb(H$_2$O)$_6$	41.10	4.55	5.550	−20.2	28

$$\Gamma = -\frac{CI_m}{\hbar\gamma}. \qquad (6.6)$$

Γ may be called the magnetorotation constant. This theoretical model for the spin-rotation interaction is not yet well developed and we have only presented a detailed mathematical model for a scalar classical version of this proposed quantum mechanical Hamiltonian.

Table III compiles literature data[6,28–30,46,48–60] of nuclear spins ranging from light to heavy isotopes in molecules for which the tensorial properties of **C** and the moments of inertia can be analyzed in a straightforward manner by virtue of their simple symmetry. Included are diatomic molecules, where both **C** and the moment-of-inertia tensor have only one nonzero component, and tetrahedral (XY_4) molecules, where the moment of inertia is isotropic. The coefficients Γ were calculated according to Eq. (6.6). The fundamental significance of Γ is evident from a comparison of the molecules SnH$_4$ and SnD$_4$, whose values of C differ by a factor of 2. This difference is entirely due to the different moments of inertia, as can be seen from the Γ coefficients, which are equal for these two molecules within the accuracy displayed in the table. Similarly, the value of C for ^{139}Sb in Sb^{14}N differs from that in Sb^{15}N by 5% but the two values of Γ differ by only 1%. In Fig. 3 the Γ coefficients are plotted
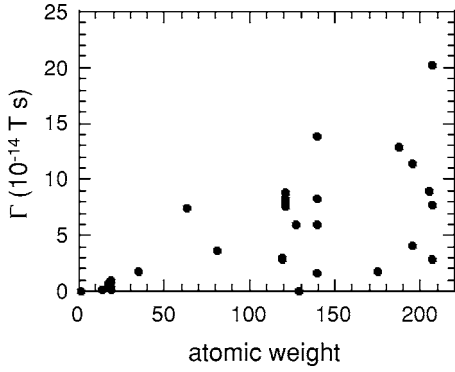
FIG. 3. The absolute values of magnetorotation constants Γ of nuclear isotopes vs their atomic weights.

against atomic weight. This plot shows that in general one expects increased magnetic effects in the heavier elements. It is most certainly a result of the greater tendency of larger electron clouds to be distorted by ligand forces.

As an aside, it is worthwhile mentioning that the combination CI_m/γ in Eqs. (6.5) and (6.6) also plays a role in Ramsey's theory[44,47] of the chemical shielding and molecular spin-rotation interactions. One outcome of this theory is that the paramagnetic portion of the chemical shielding is closely related to the spin-rotation constant. The absolute chemical shielding σ of a nucleus in a molecule can be expressed as the sum of the absolute shielding σ_{FA} of the free atom and a paramagnetic term σ'_p that is proportional to the spin-rotation constant of the molecule.[45] Using the definition of Γ introduced in Eq. (6.6), this relation is given by

$$\sigma = \sigma_{FA} + \sigma'_p = \sigma_{FA} - \frac{2\pi\mu_B}{\hbar}\Gamma, \qquad (6.7)$$

where μ_B is the Bohr magneton. The ratio of Γ and σ'_p is a universal constant that does not depend on the nature of the molecule or the nucleus. This further suggests that the magnetorotation constant Γ is at least as "fundamental" as is the spin-rotation constant C. The paramagnetic shielding σ'_p determines the local magnetic field generated by paramagnetic distortions of molecular wave functions in response to an external magnetic field, while Γ determines the local magnetic field generated by distortions of molecular wave functions in response to rotations.

Equation (6.4) is the basis for a direct nuclear spin-relaxation process, where the local magnetic field is proportional to a local angular velocity, $\Delta B_x = i_1\Omega$ [Eq. (4.17)] with $i_1 = \Gamma$. According to Eq. (4.18) its relaxation rate is

$$\frac{1}{T^{SR}_{1\text{direct}}} = \frac{2\pi\gamma^2\Gamma^2 k_B T \omega_0^4}{mv^2\omega_D^3}. \qquad (6.8)$$

For a Raman process involving the spin-rotation interaction, one needs a term in the expansion of ΔB that is second-order in the parameters that characterize the atomic displacements. If the relaxation is caused by the spin-rotation interaction, one must be the angular velocity Ω while the other may be either d, θ, or Ω. An obvious possibility is a term proportional to the square of the angular velocity. How-

ever, since we have no means of estimating the size of its coefficient, we opt to ignore its contribution in the hope that it is, indeed, negligible. As an alternative, we choose the product term of the angular velocity and the bond-distance increment, the magnitude of which we are fortunately able to estimate. It originates in the bond-length dependence of the spin-rotation constant. When an atomic separation increases from its equilibrium length, a, to $a+d$, the spin-rotation interaction decreases.[6,48,50,55] For small elongation d, this can be expressed in the linear form

$$\Gamma = \Gamma_0(1 - \varepsilon d), \qquad (6.9)$$

where ε is related to the derivative of Γ with respect to interatomic separation at equilibrium, and Γ_0 is the value of this quantity at equilibrium. The coefficient ε has been evaluated numerically for a few simple molecules (see Table IV).[6,48,50,55] Thus, one has the expansion

$$\Delta B = \Gamma\Omega = \Gamma_0\Omega - \varepsilon\Gamma_0\Omega d, \qquad (6.10)$$

where the last term is second-order in vibrational parameters because it involves the product of Ω and d. They are associated with the transverse and longitudinal vibrational modes shown in Figs. 1(d) and 1(b), respectively. Substituting $-\varepsilon\Gamma_0$ for j_2 in Eq. (4.19) gives the Raman relaxation rate,

$$\frac{1}{T^{SR}_{1\text{Raman}}} = \frac{2\pi\sqrt{2}\gamma^2 a^2 \varepsilon^2\Gamma_0^2\omega_D k_B^2 T^2}{7m^2v^4}. \qquad (6.11)$$

It is of interest to compare this result with the corresponding equation for Raman relaxation obtained by Fitzgerald *et al.*[6] derived for solid ^{129}Xe,

$$\frac{1}{T_1^S} = \frac{9\pi c_K^2 T^{*2}}{4\hbar^2\omega_D}\eta^S(\varepsilon_0, T^*). \qquad (6.12)$$

In Eq. (6.12), $c_K/\hbar$ is the spin-rotation constant of ^{129}Xe$_2$ in frequency units, T^* is the reduced temperature T/Θ_D, ε_0 is a dimensionless parameter equivalent to $-a\varepsilon$ as defined by us, and η^S is a dimensionless function that is independent of T in the high-temperature limit and is dominated by terms that are quadratic in ε_0.[6] By making the substitutions $c_K/\hbar = \hbar\gamma\Gamma_0/I_m$ [Eq. (6.6)], $I_m = ma^2/2$ (moment of inertia of Xe$_2$), $a = \pi v/\omega_D$ [Eq. (3.2) at the Debye frequency, where $\lambda \approx 2a$], and $\Theta_D = \hbar\omega_D/k_B$ [Eq. (3.3)], Eq. (6.12) becomes

$$\frac{1}{T_1^S} = \frac{9\gamma^2\Gamma_0^2\omega_D k_B^2 T^2}{\pi^3 m^2 v^4}\eta^S(-a\varepsilon, T^*). \qquad (6.13)$$

This equation has nearly the same parametric dependence on the physical constants of the material as Eq. (6.11) derived by us. The ratio of the two expressions is $\sim 0.2\eta^S(-a\varepsilon, T^*)/a^2\varepsilon^2$, which for solid ^{129}Xe is equal to about 4 in the high-temperature limit, based on the values of $\varepsilon_0 = -a\varepsilon = -11.4$ and $\eta^S = 2687$ provided by Fitzgerald *et al.*[6] The small numerical difference demonstrates that the general model developed here and that of Fitzgerald *et al.* developed for xenon are consistent with one another.

As mentioned above, our model predicts nuclear spin-lattice relaxation rates due to the interaction with a single atomic neighbor. We have not developed a method to ac-

count for multiple neighbors in a generalized relaxation model.

According to Eq. (3.15), the mean-square amplitude of angular velocities $\langle \psi(\omega)^2 \rangle$ increases quadratically with the frequency. This is in contrast to the mean-square amplitudes of the relative displacement amplitudes $\langle d(\omega)^2 \rangle$ and $\langle \chi(\omega)^2 \rangle$, which according to Eqs. (3.10) and (3.13) are independent of ω. As such, the vibrational modes close to the Debye cutoff contribute in disproportionate measure to this relaxation process. In view of the gross assumptions made in the Debye model, particularly close to the Debye frequency, where it is known that realistic crystal models deviate heavily from the ideal mode distribution,[38–40] we have reason to expect that $1/T_1$ in Eq. (6.11) may deviate substantially from the actual relaxation rate. We must, therefore, be satisfied if agreement within an order of magnitude is achieved.

The strong increase of $\langle \psi(\omega)^2 \rangle$ when the frequency approaches the Debye frequency is also the reason why the direct-process nuclear spin-lattice relaxation rate due to the spin-rotation interaction is many orders of magnitude smaller than the relaxation rate of the Raman process, as can be seen from the ratio of the $1/T_1$'s,

$$\frac{T_{1\text{direct}}^{\text{SR}}}{T_{1\text{Raman}}^{\text{SR}}} = \frac{\sqrt{2} a^2 \varepsilon^2}{7} \frac{k_B T}{m v^2} \frac{\omega_D^4}{\omega_0^4}, \tag{6.14}$$

in which the ratio $(\omega_D/\omega_0)^4$ is of the order of 10^{20}.

VII. NUMERICAL ESTIMATES OF NUCLEAR SPIN-LATTICE RELAXATION RATES

Numerical values for the nuclear spin-lattice relaxation rates derived in the previous sections can be calculated only if the physical constants used in the expressions are known. Unfortunately, many of those, in particular the magnetorotation constant Γ and the coefficient ε for its dependence on bond lengths, are generally not found in the literature. Even their orders of magnitude are largely unknown. In this section, it is shown that reasonable choices of the parameters' values give nuclear spin-lattice relaxation rates that are consistent with experimentally measured relaxation rates.

Solid ^{129}Xe, which exhibits nuclear spin-lattice relaxation behavior characteristic of a Raman process, is arguably the only compound for which the complete set of parameters needed for a theoretical evaluation of the spin-rotation relaxation rate is available. The formalism of Fitzgerald *et al.* ($c_K/h = 27$ Hz, $\eta^S = 2686.8$, $\Theta_D = 55$ K) yielded a value of $A = 2.2 \times 10^{-8}$ s^{-1} K^{-2} for the coefficient of the T^2 dependence of $1/T_1$ in Eq. (1.1), in near-perfect quantitative agreement with experiment.[6] More recently, independently calculated values of the spin-rotation constant for Xe$_2$ at various bond lengths have become available,[55] as well as new experimental results for the sound velocity in solid Xe.[61] They offer an opportunity to verify the accuracy of the expression for the relaxation rate proposed in the present work. The spin-rotation constant calculated by Hanni *et al.*[55] at bond distances of $r = 3$, 4.36, and 6 Å can be fitted to an exponential curve $C[\text{kHz}] = (0.0302) \exp[-2.64(r[\text{Å}] - 4.36)]$, from which one derives $\Gamma_0 = 4.8 \times 10^{-16}$ T s and $a\varepsilon = 11.8$ at the equilib-

TABLE IV. Bond-length dependence of the spin-rotation constant, $C = C_0 (1 - \varepsilon d)$, d being a small bond-length deviation from the equilibrium length a.

Molecule	a (Å)	C_0 (kHz)	ε (Å^{-1})	Reference
^{1}H$_2$	0.741	118.18	4.79	48
^{17}O$_2$	1.207	22.0136	1.00	50
^{129}Xe$_2$	4.36	0.0302	2.65[a]	55
^{129}Xe solid	4.4	−0.027	2.6[b]	6

[a]From fit of C to $0.0302 \times \exp[(-2.64)(d)]$.
[b]Derived from the product $a\varepsilon$, designated by Fitzgerald *et al.* as $-\varepsilon_0$ (Ref. 6).

rium distance $r = 4.36$ Å. This value of $a\varepsilon$ is in remarkable agreement with Fitzgerald *et al.*'s value of -11.5 for ε_0, the definition of which is equivalent to that of $-a\varepsilon$. The sound velocity v was reported to range between 0.65×10^3 and 1.45×10^3 m/s for xenon.[61] The Debye temperature of 55 K corresponds to $\omega_D = 6.8 \times 10^{12}$ s^{-1}. Substitution of these parameters in Eq. (6.11) gives $A = 0.6 \times 10^{-8}$ s^{-1} K^{-2}, a result that differs by only a factor of 4 from the reported A coefficient for solid xenon.

As a check for the order-of-magnitude agreement between the model developed here and the experimentally determined nuclear spin-lattice relaxation rates for heavy nuclei, we substitute in Eq. (6.11) parameter values that may reasonably be expected to hold for lead nitrate. The Debye temperature is 198 K,[62] corresponding to $\omega_D = 2.45 \times 10^{13}$ s^{-1}. Furthermore, the (anisotropic) velocity of sound is between 5 and 10 $\times 10^3$ m/s.[63] The Pb-O distance is $a = 2.8$ Å (Ref. 64) and the average atomic weight is 37 times that of the proton, corresponding to a ratio $k_B T/m v^2 \sim 1.0 \times 10^{-3}$ at room temperature. If we further choose $\Gamma_0 = -10 \times 10^{-14}$ T s and $\varepsilon = 3.5$ Å^{-1} (estimates that are not unreasonable in comparison with other compounds listed in Tables III and IV), we obtain $T_{1\text{Raman}}^{\text{SR}} = 10$ s at room temperature, in excellent agreement with the experimental value of 8 s.[15] Likewise, we can choose appropriate values of Γ_0 and ε that give relaxation times in agreement with measured T_1's for the other lead compounds listed in Table I. However, a quantitative explanation for the T_1 variation among the lead compounds cannot be given at the present time.

Although it is well known that Raman-relaxation rates mediated by dipolar interactions are much too small to explain even the longest measured T_1's,[22] it is of interest to estimate it for ^{207}Pb relaxation in PbCl$_2$, the Pb compound listed in Table I having the strongest dipolar interaction. As reported elsewhere,[14] its T_1 is 10 s at room temperature. For order-of-magnitude purposes, we use the same crystallographic and thermodynamic parameters as quoted above for Pb(NO$_3$)$_2$. Substituting those and the appropriate γ's in Eq. (5.5) yields a T_1 of the order of 10^{12} s ($\sim 30\,000$ years).

^{203,205}Tl spin relaxation can be understood in a qualitative sense as its magnetorotation constants and relaxation rates are both comparable with those of ^{207}Pb (Tables I and III). The preliminary result, quoted in Table I, of a somewhat longer T_1 for ^{119}Sn agrees equally well with the general trend of diminishing magnetorotation constant with decreasing

atomic weight. As mentioned in the discussion of Table I in the Introduction, the Raman-process relaxation rates of ^{111,113}Cd (Refs. 4 and 5) and of ^{109}Ag (Refs. 1 and 2) are very small, while ^{199}Hg results are inconclusive as to the contribution of the Raman process. We are presently not in a position to test the validity of our theory against observed relaxation behavior, as no spin-rotation constants are known for ^{199}Hg and ^{111,113}Cd to the knowledge of the authors. Likewise, the upper limit for the spin-rotation constant of ^{109}Ag that can be deduced from the absence of corresponding hyperfine splittings in rotational spectra of noble-gas adducts of Ag halides[53,65,66] is too large to explain the very long relaxation times of that nucleus. For the heavy spin-1/2 nuclei ^{183}W, ^{111}Os, and ^{195}Pt, no nuclear spin-lattice relaxation rates in solids could be found so we cannot comment on the applicability of our model for compounds with these nuclei.

VIII. DISCUSSION AND SUMMARY

We have presented a theory for the nuclear spin-lattice relaxation of spin-1/2 nuclei via a Raman process enabled by the spin-rotation interaction. Despite the many approximations in the development of the model and in the numerical evaluations of the relaxation rate, the proposed mechanism seems to be a viable candidate for the explanation of the observed nuclear spin-lattice relaxation rates of heavy spin-1/2 nuclei in crystalline solids. Before we began the present work, strong indications for a spin-rotation Raman process had already been identified by Grutzner *et al.*[15] The main contribution of the current paper is that it corroborates this proposition by identifying a specific mechanism of magnetic coupling between the spins and the lattice vibrations that predicts the relaxation rates in a semiquantitative manner. A similar mechanism had been evoked to explain the nuclear spin-lattice relaxation rate of solid ^{129}Xe.[6] As required for the proper functioning of a Raman process, the coupling responsible for the relaxation is a second-order magnetic perturbation proportional to the product of two geometric lattice-fluctuation parameters. In the proposed mechanism, one is the small-angle rotational motion of atomic groups and the other is a vibrational motion that causes a local structure deformation.

In our approach, the fluctuating local magnetic field responsible for the spin relaxation is described in terms of amplitudes and mode densities of a classical frequency-mode model. This model leads directly to expressions for the spectral density and for $1/T_1$, Eqs. (2.9) and (2.10). The frequency modes of the magnetic field are derived from the Debye model of vibrational lattice modes. Above the Debye temperature, the vibration amplitudes are determined by the equipartition theory, which is directly responsible for the T^2 dependence of the relaxation rates. The frequency-mode approach has the advantage that it facilitates a physically transparent description of the lattice motions. This is apparent in the way we are able to differentiate between the effects of various types of vibrational modes on motions of atoms relative to each other. It proved to be particularly useful for a quantitative assessment of angular velocities of atoms pairs, which can readily be treated by taking the time derivatives of classical expressions for atomic displacements.

Our theory expands the usual application of the spin-rotation interaction through introduction of a "magnetorotation constant" Γ. It relates the spin-rotation-induced magnetic field at the site of a nucleus to the angular *velocity* of the rotating molecular entity, in contrast to the spin-rotation constant C, which relates the spin-rotation interaction to the angular *momentum*. In freely rotating molecules, Γ and C are related through $\hbar\gamma\Gamma = CI_m$, where I_m is the moment of inertia. In Sec. VI several virtues of Γ were pointed out, prompting us to believe that Γ may be a more "fundamental" physical parameter than C. Since the angular velocity is a more adequate parameter for the description of relative motions in a small structural element of a vibrating crystal than is the angular momentum, we preferred to work with Γ. It is also the most appropriate physical property to serve as a link between spin-rotation interactions in solids and in small molecules. As such it provides a means for estimating the size of the effect in solids. Fortunately for our purpose, there is an increased availability of spin-rotation constants of heavy nuclear spins in recent years, thanks to recent improvements in the instrumentation used for molecular spectroscopy.[66] However, the theoretical model for the spin-rotation interaction in vibrating solids is not yet well developed and we have only attempted to present an estimate of a physical effect that actually requires to be investigated in a full quantum mechanical model.

Since the spin-rotation relaxation theory presented in this paper is derived under several simplifying assumptions, it must be considered as being in its infancy. Among the approximations are the adoption of the Debye model for acoustical vibrational modes and the neglect of optical vibrational modes. Furthermore, when describing the effects of strain on the size of the magnetorotation constant, we considered changes in atomic distances but ignored bending deformations. We have also neglected cumulative effects of multiple neighbors in the coordination sphere. An additional difficulty in a quantitative evaluation of the nuclear spin-relaxation rate is the uncertainty in the values of physical parameters to be substituted in the $1/T_1$ equation, in particular those of the magnetorotation constant Γ and the parameter ε quantifying its dependence on atomic distances.

For ^{207}Pb and ^{199}Tl, estimates of magnetorotation constants and of their derivatives with respect to the interatomic distance, in line with corresponding values of molecules in the gas phase, successfully predict the efficient relaxation found for lead and thallium compounds. For solid ^{119}Xe we obtained surprisingly good agreement with published experimental data, based on recently reported physical properties of the parameters entering the equation of $1/T_1$. However, the observed Raman relaxation rates for ^{113}Cd and ^{109}Ag are unobservably small in compounds of these nuclei, and we hope that the appropriate spin-rotation constants, when measured, will be consistent with this finding. An encouraging finding is that the magnetorotation constants of the heavy elements tend to increase with increasing atomic weight (Table III and Fig. 3). It agrees favorably with the prevalence of Raman relaxation in the heaviest nuclei. At the same time, it is seen that magnetorotation constants of a particular nucleus can change dramatically from compound to com-

pound. This could be the reason why the spin-lattice relaxation times of ^{207}Pb tabulated in Table I range over more than an order of magnitude. Quantum-mechanical calculations of the electronic structures are probably the only means for obtaining specific explanations of this behavior.

In the Introduction, we referred to the nuclear spin-rotation relaxation mechanism in liquids, which sometimes implies an evaluation of the collisional correlation times in the 10^{-14} to 10^{-13} s range. Such short correlation times are shorter than a typical vibration period and are therefore difficult to envision. It suggests that the spin-rotation model in liquids needs to be revised. Borrowing from the concepts developed in this paper, we speculate that the observed relaxation process in those liquids is due to simultaneous fluctuations of angular velocities and molecular deformation brought about by collisions with other molecules. Unfortunately, we have no knowledge of statistical models that quantitatively describe such dynamic processes in liquids in a manner analogous to the Debye model of lattice vibrations. We have, therefore, no mechanism in place that would facilitate the implementation of this idea in a practical relaxation model for liquids.

This work has shown that the spin-lattice relaxation rates of the heavy elements contain information about the lattice dynamics of the crystals that contain them and, through their spin-rotation properties, about their electronic structure. We hope that these results will encourage others to improve our theoretical understanding of the relaxation process and to develop solid-state NMR techniques for measuring the temperature dependence of $1/T_1$ in compounds containing nuclei listed in Table I.

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