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Nuclear quadrupole spin-lattice relaxation in anharmonic molecular crystals

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An approach for nuclear quadrupole spin relaxation by anharmonic lattice vibrations of quadrupole nuclei situated at molecular or ion groups is presented. The temperature dependence at constant crystalline configuration is analyzed. This approach takes advantage of the existence of tightly bound molecules or molecular groups. Fluctuations causing relaxation are considered as collective vibrations of the whole lattice. Anharmonicity is explicitly included by involving cubic and quartic terms of the lattice vibrations Hamiltonian. The spectral densities of the spin-lattice Hamiltonian are expressed in terms of the phonon spectral densities and the temperature Green-function perturbation formalism is used for calculating the lower-order contributions. Three kinds of processes are found to contribute mainly to the spin-lattice relaxation time (T_1), namely, anharmonic Raman (AR), first-order Raman (1R), and a third mechanism originated in the self-energy effects on the two-particle spectral density. The AR and 1R processes yield a quadratic temperature dependence of T_1 while the third mechanism gives a cubic temperature dependence. This last term, being characteristic of molecular crystals, represents a sort of mixing of the AR and 1R mechanisms, and its influence strongly depends on the crystal symmetry.

I. INTRODUCTION

One of the most important mechanisms contributing to nuclear spin-lattice relaxation in molecular crystals is the one driven by the fluctuations of the interaction of the nuclear quadrupole with the electric-field gradient existing at the nuclei site. Commonly, at intermediate temperatures the coupling between nuclear transitions and the normal lattice vibrations constitutes the dominant mechanism.[1]

Pure NQR measurements of the spin-lattice relaxation time, T_1, as a function of temperature and pressure give information about the fluctuational spectrum associated with vibrations of the molecules in molecular crystals. However, at the present status of the theory, it is not possible to relate directly the experimental T_1 data with the dynamical properties of the lattice because the dynamic nature of molecular vibrations is included in an averaged way, as in a mean-field approach. For example, processes with a local character cannot be distinguished from those related with intermolecular correlations.

At the present there are two kinds of approaches for T_1 in crystals due to thermal vibrations. They were conceived for very different kinds of crystals and represent two well-distinct limits. One of them deals with ionic crystals in which the resonant nuclei lie on monoatomic-like sites. NQR spin-lattice relaxation in these crystals is described by Van Kranendonk's model:[2] the quadrupole interaction depends, in principle, on the instantaneous displacements of all atoms of the crystal. The components of the EFG tensor are expanded in terms of the lattice phonons and the spectral densities of the spin-lattice interaction Hamiltonian are calculated by means of the Green-function formalism. This theory yields a quadratic temperature dependence for T_1 for above the Debye temperature[3] which generally verifies in this kind of crystal, for high temperatures.

The other approach refers to molecular crystals where the resonant nuclei belong to a molecular group or ion whose atoms are tightly bound by covalents bonds, while the intermolecular forces are less intense. The shapes and sizes of the molecules forming molecular crystals are nearly the same of the gaseous state. Because of the complexity of the lattice dynamics of molecular crystals, the spin-lattice relaxation has been described by a rather different approach based on a molecular viewpoint.[4,5] Models of this kind are based on the assumption that the main contribution to the EFG fluctuations comes from the motions of the molecule bearing the resonant nucleus. This decisive hypothesis was first formulated by Bayer[6] for nuclear relaxation in molecular crystals and all the later descriptions for the temperature dependence of T_1 and the NQR frequency rely on this basic assumption. Such models assume that the molecule makes transitions among discrete torsional oscillation levels, but the nature of the interactions producing the molecular transitions is not analyzed. Instead, T_1 is calculated in terms of an average lifetime of the molecular torsional states, through a stochastic model of uncoupled harmonic oscillators.[4,5] The general temperature dependence so obtained may be expressed as $T_1^{-1} = AT^{\lambda}$ with $\lambda \simeq 2$.[7]

A theoretical review of the existent models for relaxation in molecular crystals becomes necessary in order to account for a great volume of experimental data showing noticeable discrepancies of the temperature dependence with respect to the predicted behavior. Besides, a more detailed knowledge about the role that anharmonic interactions play in the spin-lattice relaxation phenomena would be helpful whenever molecular order becomes an important feature.

There exist too many examples in which departures from the quadratic power law are observed. In many cases the data follow a T^{λ} law, λ being even greater than three.[8,9] It is impossible to account for such a behavior starting from the semiclassical available models. In other cases, the rate of the decrease of T_1 with temperature shows a monotonous enhancement even in a logarithmic plot (see, for example, Refs. 10 and 11). In some cases this behavior is ascribed to anharmonicity of the molecular motions, but it is not clear how to include it in the model.[11] Departures of the experimental data from the quadratic temperature law are also frequently ascribed to relaxation mechanisms other than vibrations, such as thermally activated processes[4] or pretransition effects.[10] Their influence in the relaxation rates is usually considered as independent from vibrations. Even if such an assumption holds, it might not be accurate to represent the vibrational mechanism with a power law with a constant value for the exponent (λ), because this temperature dependence was deduced by disregarding the anharmonic intermolecular correlations.

In the limit of molecular crystal, the direct intermolecular contribution to the fluctuation spectrum can be neglected when compared with the intramolecular one. This assumption is meaningful because the most important contribution to the EFG value generally comes from the molecule bearing the resonant nucleus. For example, the field gradient at the chlorine nucleus in both sodium chlorate and potassium chlorate is due primarily to the electron distribution at the chlorate ion, and is almost unaffected by changes in molar volume. A calculus of the EFG at the chlorine site in sodium chlorate[12] shows that the intermolecular contribution is not greater than one-hundredth of the intramolecular contribution. In this example the lattice sums calculated with a point charge model converge when atoms within a 50-Å sphere are considered. In the *p*-chloronitrobenzene crystal a calculus of the external contribution to the EFG at the chlorine sites was made by assuming the molecular charge distribution as dipoles.[14] In this case the lattice sum converges within a sphere of three-unit-cell radius, yielding a value for the intermolecular contribution of only 2% of the intramolecular one.

An estimation of the contribution to the ^{35}Cl spin-lattice relaxation due to the motion of the sodium neighboring atoms in $NaClO_3$ was reported by Weber.[15] He argues that the fluctuating EFG responsible for the chlorine relaxation arises principally from the charge motion within the chlorate ion. By using the Van Kranendonk theory he concludes that the contribution coming from the six-nearest-neighboring ions is several orders of magnitude smaller than the intramolecular contribution. All the arguments enumerated above induce us to think that a model which disregards the *direct intermolecular* contributions to T_1 would apply to a wide class of molecular crystals where the resonant nucleus is tightly bound to the molecular group.

Under these assumptions the time dependence of the EFG at the nucleus site can be written in terms of the Euler angles describing the orientation of the principal EFG axes, the value of its *z-z* component, V_{zz} and the asymmetry η.[13] The intramolecular charge distribution defines the coordinate axis where the EFG tensor can be diagonalized and it is assumed that the principal term "follows" the atomic motions. If the direct intermolecular fluctuations were important, this description would not be correct any more, and the instantaneous displacements of all atoms should be considered, as in the theory for monoatomic-like crystals.[2]

The present work focuses on the NQR spin-lattice relaxation for nuclear spin $I=\frac{3}{2}$ in the limit of molecular crystals. The collective character of the molecular motions is explicitly included through the formalism for lattice dynamics of molecular crystals.[16,17] By describing quantum mechanically both the spin system and the lattice, we include in an explicit way the intermolecular correlations due to the anharmonicity of the crystalline field of forces. It is at this point that the present work goes a step further with respect to the previous models for spin-lattice relaxation in molecular crystals.

Anharmonicity was explicitly included by involving cubic and quartic terms of the lattice vibrations Hamiltonian. The spectral densities of the spin-lattice Hamiltonian were expressed in terms of the phonon spectral densities. By using the Green-function formalism the contributions to T_1^{-1} from the anharmonic-Raman (AR) and first-order-Raman (1R) processes were calculated. They both contribute with quadratic terms to the temperature dependence. We found that the lower-order contribution to the spectral density related to nuclear spin transitions with $\Delta m=1$, W_1, originate in the coupling between these transitions and three phonon processes. This coupling (AR) being driven by the cubic terms of the vibrational Hamiltonian cannot be represented by a single correlation time. On the other hand, the first-order contribution to W_2 ($\Delta m=2$) comes from the coupling with harmonic processes of two phonons (1R) and it admits the definition of a global lattice correlation time. The second-order contribution to W_2 arises from the self-energy effects on the two-particle spectral densities. These processes, which can be thought of as interactions between the AR and 1R contributions, yield a cubic temperature dependence and could account for some departures of data from the semiclassical models. Summarizing, our analysis showed that the fluctuation spectra related with W_1 have a different character than the one related with W_2.

For the sake of simplicity we first analyzed in detail the case of a symmetric EFG tensor, $\eta=0$. The consequences of including a parameter $\eta\neq0$ were evaluated in a separate section. We found that the inclusion of the EFG asymmetry does not produce relevant differences with the case of $\eta=0$.

II. SPIN-LATTICE RELAXATION

In this work we study the nuclear spin relaxation by lattice vibrations of quadrupole nuclei situated at molecular or ion groups. In these cases, relaxation is mainly driven by the fluctuations in the quadrupolar interaction resulting from the motions of the molecular group bearing the resonant nucleus. As discussed in the Introduction, we neglect the fluctuations of the quadrupole interaction coming directly from the motions of the neighboring groups. We instead focus the description in the collective nature of the molecular motions.

The Hamiltonian for the interaction of an electric quadrupole moment of a nucleus with the electric-field gradient, EFG, at the nucleus site is[18]

$$\mathcal{H}_Q=\sum_{M=-2}^{2}(-1)^M F^{\mathrm{cr}}_{2,-M}Q_{2,M}\ , \tag{1}$$

where $Q_{2,M}$ denote crystal frame spin operators. For spin $I=\frac{3}{2}$

$$Q_{2,0}=\frac{eQ}{6}(3I_z^2-\mathbf{I}\cdot\mathbf{I}),\quad Q_{2,\pm1}=\frac{eQ}{2\sqrt{6}}(I_\pm I_z+I_z I_\pm)\ ,$$
$$Q_{2,\pm2}=\frac{eQ}{2\sqrt{6}}I_\pm I_\pm\ , \tag{2}$$

and F^{cr}_{2-M} are the elements of the electric-field gradient in the crystal frame. The EFG at the nucleus is mainly due to the electrons in the bond, and fluctuates in orientation in the spin-fixed axis system (crystal frame) due to molecular tumbling. When expressed in the bond fixed principal frame, the EFG elements can be specified by its asymmetry parameter, η, and q, the component of the EFG tensor along the z^b axis[18]

$$F_0^b=eq/2,\quad F^b_{\pm1}=0,\quad F^b_{\pm2}=\eta eq/(2\sqrt{6})\ . \tag{3}$$

The crystal frame is chosen so that it coincides with the molecular bond frame when the molecule is at the equilibrium position.

The coupling of the nuclear spin system with the lattice originates in the time fluctuations of the quadrupole Hamiltonian. The time dependence of the quadrupole interaction energy may be obtained by transforming the EFG tensor from the bond fixed frame to the crystal frame according to

$$F^{\mathrm{cr}}_M=\sum_{N=-2}^{2}D^{(2)}_{NM}(\Omega)F^b_N\ , \tag{4}$$

where $D^{(2)}_{NM}$ are the second rank Wigner matrix elements[19] and Ω represents the time-dependent Euler angles of the transformation: α, ϕ, and θ. These angles correspond to rotations about the space-fixed axes z^b, y^b, and z^b, respectively. [In writing Eq. (4) we have assumed that rigid and intramolecular motions are uncorrelated. Otherwise a first step transforming from the bond frame to the molecular frame would be necessary.] The second-rank Wigner matrices take the following general form:

$$D^{(2)}_{NM}(\alpha,\phi,\theta)=e^{-iM\alpha}e^{-iN\phi}d^{(2)}_{NM}(\theta) \tag{5}$$

with N and $M=0,\pm1,\pm2$.

We assume that the probabilities of occupation of the spin states, $P_n(t)$, satisfy a master equation

$$\frac{dP_n}{dt}=\sum_m[P_m W_{mn}-P_n W_{nm}]\ . \tag{6}$$

The probabilities per unit time, $W_{mm'}$, of a transition from state m at $t=0$ to state m' at time t involved in Eq. (6) are time independent; these quantities can be obtained from a perturbative expansion of the density matrix up to second order:[20]

$$W_{mm'}=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}G_{m'm}(t)e^{-i\omega_Q t}dt\ , \tag{7}$$

$G_{m'm}$ being the correlation function of the quadrupolar Hamiltonian

$$G_{m'm}(t)=\langle\mathcal{H}_{Qm'm}(t)\mathcal{H}^*_{Qmm'}\rangle\ . \tag{8}$$

The brackets in the last equation indicate the statistical ensemble average. The off-diagonal matrix elements of the quadrupole Hamiltonian in the crystal frame $\mathcal{H}_{Qm'm}$ are[4]

$$\langle m\pm1|\mathcal{H}_Q|m\rangle=eQ/12(2m\pm1)[(\tfrac{3}{2}\mp m)(\tfrac{5}{2}\pm m)]^{1/2}F^{\mathrm{cr}}_{\mp1}\ ,$$
$$\langle m\pm2|\mathcal{H}_Q|m\rangle=eQ/24[(\tfrac{1}{2}\mp m)(\tfrac{3}{2}\mp m)(\tfrac{5}{2}\pm m)(\tfrac{7}{2}\pm m)]^{1/2}F^{\mathrm{cr}}_{\mp2}\ . \tag{9}$$

It can be seen from Eq. (6) that for $I=\frac{3}{2}$, the spin-lattice relaxation time satisfies the following relation in terms of the transition probabilities per unit time:

$$T_1^{-1}=2(W_1+W_2)\ , \tag{10}$$

where we defined

$$W_1\equiv W_{3/2,1/2},\quad W_2\equiv W_{3/2,-1/2} \tag{11}$$

for nuclear transitions with $\Delta m=1$ and $\Delta m=2$, respectively.

Finally, by use of Eqs. (7)–(9) the following expressions for the transition rates can be obtained:

$$W_j=\frac{1}{12j^2}\left[\frac{eQ}{\hbar}\right]^2\int_{-\infty}^{\infty}\langle F^{\mathrm{cr}}_j(t)F^{\mathrm{cr}*}_j\rangle e^{-i\omega_Q t}dt \tag{12}$$

with $j=1$ or 2; and inserting Eqs. (3) and (4) we write these functions in terms of the Wigner matrices of second rank. After considering the EFG parameters q and η as time independent we obtain [considering q and η as time-dependent yield corrections of higher order than those of Eq. (13)]

$$\langle F^{\mathrm{cr}}_j[\Omega(t)]F^{\mathrm{cr}*}_j\rangle=F_0^{b2}\langle\{D_{0,j}[\Omega(t)]+\eta/\sqrt{6}D_{-2,j}[\Omega(t)]+\eta/\sqrt{6}D_{2,j}[\Omega(t)]\}[D^*_{0,j}(\Omega)+\eta/\sqrt{6}D^*_{-2,j}(\Omega)$$
$$+\eta/\sqrt{6}D^*_{2,j}(\Omega)]\rangle\ . \tag{13}$$

The angular orientation of the principal term depends on the instantaneous configuration of the molecular group. The lattice dynamics of a molecular crystal is more conveniently described in terms of molecular coordinates rather than in terms of atomic displacements because in this way it is possible to take advantage of the existence of tightly bound molecular groups (ions or molecules). When the intramolecular interactions are sufficiently strong as compared with the crystalline ones, it is meaningful to separate the dynamical problem into two well-distinct parts: one relative to the external and one to the internal vibrations. This assumption is known as the *rigid-body approximation.* External motions are the rigid-body translations of molecules and the rotations around the principal axes of inertia. The internal motions instead involve distortions of the molecule and are mainly governed by the intramolecular forces; the interactions with other molecular groups are only small perturbations. The internal frequencies are generally independent of the wave vector; in contrast, the external motions exhibit important anharmonicity and dispersion.

The spatial configuration of the molecular groups can be described, to first order in the amplitudes of the molecular motions, by uncoupled molecular coordinates corresponding to rigid translations and rotations and internal distortions.[16] We find it useful to expand the Wigner matrices in terms of these coordinates as a first step in writing the EFG tensor in terms of collective coordinates of the lattice. At this stage we have introduced the lattice dynamics into the description of the temperature dependence of the spin-lattice relaxation time.

For small values, the Euler angles can be written as linear functions of the molecular coordinates q_s:

$$\theta=\sum_s a_s q_s, \quad \theta=\sum_s b_s q_s, \quad \alpha=\sum_s c_s q_s \ , \tag{14}$$

where $a_s \equiv [\partial\theta/\partial q_s]_{q_s=0}$ represents the sensibility of θ due to the sth molecular displacement q_s, a similar definition holds for b_s and c_s.

The Wigner matrices can be assumed to depend on the molecular coordinates through their dependence on the Euler angles. Generally we can write

$$F_M^{\mathrm{cr}}=F_M^{\mathrm{cr}}[\phi\{q_s\},\theta\{q_{s'}\},\gamma\{q_{s''}\}] \ , \tag{15}$$

where the symbols $\{q_s\}$ represent the sets of molecular coordinates producing the time dependence of the Euler angles. In the case of small amplitude angles we represent these functions by their Taylor expansions in terms of $\{q_s\}$ around the molecular equilibrium positions, $\{q_s=0\}$. In first place we consider the case of $\eta=0$.

A. The case of $\eta=0$

When $\eta=0$ the time correlation functions associated to nuclear transitions with $\Delta m=1$ and $\Delta m=2$ from Eq. (13) reduce to

$$\begin{aligned} K_j(t) &\equiv \langle F_j^{\mathrm{cr}}[\Omega(t)]F_j^{\mathrm{cr}*}(\Omega)\rangle \\ &= F_0^{b2}\langle D_{0j}[\Omega(t)]D_{0j}^{*}(\Omega)\rangle \end{aligned} \tag{16}$$

for $j=1,2$. In this case the argument Ω in the Wigner matrices represent the azimuthal and the polar Euler angles ϕ and θ. For small θ,[19]

$$\begin{aligned} D_{0,1}(\theta,\phi)&=d_{01}(\theta)e^{-i\phi}\simeq\frac{\sqrt{6}}{2}(\theta-\theta^3/6)e^{-i\phi} \ , \\ D_{0,2}(\theta,\phi)&=d_{02}(\theta)e^{-2i\phi}\simeq\frac{\sqrt{6}}{4}(\theta^2+\theta^4/3)e^{-2i\phi} \ . \end{aligned} \tag{17}$$

After introducing the dependence of these matrices on the molecular coordinates they can be expanded in series of $\{q_s\}$:

$$\begin{aligned} D_{01}(\theta\{q_s\},\phi\{q_{s'}\}) \simeq{}& \sum_s \left[\frac{\partial D_{01}}{\partial\theta}\frac{\partial\theta}{\partial q_s}\right]_{\theta,\phi=0} q_s \\ &+\sum_{s'}\left[\frac{\partial D_{01}}{\partial\phi}\frac{\partial\phi}{\partial q_{s'}}\right]_{\theta,\phi=0} q_{s'}+\cdots \ . \end{aligned} \tag{18}$$

Then, according to Eqs. (14), (17), and (18),

$$\begin{aligned} &D_{01}(\theta\{q_s\},\phi\{q_{s'}\}) \\ &\quad=\frac{\sqrt{6}}{2}\left[\sum_s a_s q_s-\sum_{ss's''}a_s a_{s'} a_{s''} q_s q_{s'} q_{s''}+\cdots\right] \ . \end{aligned} \tag{19}$$

After replacing Eq. (19) into Eq. (16), the correlation function $K_1(t)$ becomes

$$\begin{aligned} K_1(t)&=\tfrac{3}{2}F_0^{b2}\left[\sum_{ss'}a_s a_{s'}\langle q_s(t)q_{s'}^{*}\rangle+\tilde{k}_1\right]+O(q^6) \\ &=\tfrac{3}{2}F_0^{b2}[k_1+\tilde{k}_1]+O(q^6) \ , \end{aligned} \tag{20}$$

where $\tilde{k}_1$ contains terms having the following structure:

$$\sum_{\{s\}}a_s a_{s'} a_{s''} a_{s'''}\langle q_s(t)q_{s'}^{*}q_{s''}^{*}q_{s'''}^{*}\rangle$$

and $\{s\}$ stands for the set of molecular coordinate indexes $\{ss's''s'''\}$. In Appendix B we show that the contribution of $\tilde{k}_1$ to the relaxation rate is negligible compared with the one arising from the first term of Eq. (20).

Similarly, the correlation function related to $\Delta m=2$ is

$$K_2(t)=\tfrac{3}{8}F_0^{b2}\sum_{\{s\}}a_s a_{s'} a_{s''} a_{s'''}\langle q_s(t)q_{s'}(t)q_{s''}^{*}q_{s'''}^{*}\rangle+O(q^6) \ . \tag{21}$$

The crystalline character of the spin-lattice relaxation is better reflected by introducing lattice normal coordinates because the dynamics of the external molecular coordinates is governed by intermolecular interactions. The collective nature of the molecular vibrations becomes apparent by transforming from the normal molecular coordinates $\{q_s\}$ to a set of crystalline coordinates $Q_{\mathbf{k}j}$. Finally, by introducing the quantum creation and annihilation operators into the description

$$A_{\mathbf{k}j}\equiv(a_{-\mathbf{k}j}^{\dagger}+a_{\mathbf{k}j}) \tag{22}$$

a general expression for the molecular coordinates can be obtained,[16]

$$q_s=\sqrt{\hbar/2L}\sum_{\mathbf{k}j} v(s|\mathbf{k}j)\omega_{\mathbf{k}j}^{-1/2}A_{\mathbf{k}j}e^{i\mathbf{k}\cdot\mathbf{R}_0}\ , \tag{23}$$

where $v(s|\mathbf{k}j)$ are the eigenvectors of the dynamical matrix and $\mathbf{R}_0$ is the equilibrium position vector of the resonant nucleus.

By replacing Eq. (23) into Eqs. (20) and (21) the time correlation functions become

$$\begin{aligned} K_1&=\tfrac{3}{2}F_0^{b2}\left[\frac{\hbar}{2L}\right]\sum_{ss'}\sum_{\mathbf{k}j,\mathbf{k}'j'} a_s a_{s'} v(s|\mathbf{k}j)v^*(s'|\mathbf{k}'j')(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'})^{-1/2}\langle A_{\mathbf{k}j}(t)A^*_{\mathbf{k}'j'}\rangle\ ,\\ K_2&=\tfrac{3}{8}F_0^{b2}\left[\frac{\hbar}{2L}\right]^2\sum_{\{s\}}\sum_{\mathbf{k}j\mathbf{k}'j'\tilde{\mathbf{k}}\tilde{j}\tilde{\mathbf{k}}'\tilde{j}'} v(s|\tilde{\mathbf{k}}\tilde{j})v(s'|\tilde{\mathbf{k}}'\tilde{j}')v^*(s''|\mathbf{k}j)v^*(s'''|\mathbf{k}'j')\\ &\qquad\times a_s a_{s'} a_{s''} a_{s'''}\langle A_{\tilde{\mathbf{k}}\tilde{j}}(t)A_{\tilde{\mathbf{k}}'\tilde{j}'}(t)A^*_{\mathbf{k}j}A^*_{\mathbf{k}'j'}\rangle(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}\omega_{\tilde{\mathbf{k}}\tilde{j}}\omega_{\tilde{\mathbf{k}}'\tilde{j}'})^{-1/2}\ . \end{aligned} \tag{24}$$

B. Calculation of W_1

To progress in the calculation of W_1 and W_2 of Eq. (12) in terms of the phonon spectral densities, we have to perform the Fourier transform of K_1 and K_2 for an anharmonic lattice. To do this we use the temperature Green function (TGF) formalism.[21] This perturbative formalism constitutes a very general method which covers not only cases of low anharmonicity, but also situations of large amplitudes of atomic vibrations. This procedure allows the calculation of the temperature dependence of the successive orders in a perturbative parameter.

The spectral density of K_1 contains one-phonon spectral densities. This function can be calculated by using their known relation with the TGF

$$\begin{aligned} f^1_{\mathbf{k}jj'}(\omega)&\equiv\mathcal{F}\{\langle A_{\mathbf{k}j}(t)A^*_{\mathbf{k}'j'}\rangle\}\\ &=\frac{2\beta\hbar}{1-e^{-\beta\hbar\omega}}\lim_{\nu\to 0}\operatorname{Im}G_{\mathbf{k}j}(i\omega_n)\ , \end{aligned} \tag{25}$$

where $\mathcal{F}$ stands for Fourier transform and $G_{\mathbf{k}j}$ is the one-phonon TGF. This function is defined on the imaginary axis of the complex plane for discrete frequency values $w=i\omega_n=i2\pi n/\beta\hbar$ with an n integer. To obtain the spectral density it is necessary to make an analytic prolongation over the whole complex plane $w=\omega\pm i\nu$ and then to take the limit for real values ($\nu\to 0$).

In order to take into account the lower-order contributions to T_1 due to the anharmonicity of the crystalline potential, we consider the lattice vibrations Hamiltonian up to the quartic term in the phonon operators[16]

$$\mathcal{H}_{\text{vib}}=\mathcal{H}_0+\mathcal{H}_3+\mathcal{H}_4\ , \tag{26}$$

where

$$\begin{aligned} \mathcal{H}_0&=\sum_{\mathbf{k}j}\hbar\omega_{\mathbf{k}j}(n_{\mathbf{k}j}+\tfrac{1}{2})\ ,\\ \mathcal{H}_3&=\sum_{jj_1j_2}\sum_{\mathbf{k}\mathbf{k}_1\mathbf{k}_2}B_3\begin{bmatrix} j & j_1 & j_2\\ \mathbf{k} & \mathbf{k}_1 & \mathbf{k}_2\end{bmatrix}A_{\mathbf{k}j}A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}\ ,\\ \mathcal{H}_4&=\sum_{jj_1j_2j_3}\sum_{\mathbf{k}\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}B_4\begin{bmatrix} j & j_1 & j_2 & j_3\\ \mathbf{k} & \mathbf{k}_1 & \mathbf{k}_2 & \mathbf{k}_3\end{bmatrix}A_{\mathbf{k}_j}A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}A_{\mathbf{k}_3j_3}\ . \end{aligned} \tag{27}$$

For ordering the successive contributions to the spectral densities, it is convenient to define a perturbative parameter as the quotient between the root mean square of the angular displacement and the nearest-neighbor distance, $\epsilon=\sqrt{\langle\theta^2\rangle}/R$.[22] The order of magnitude of the anharmonic coefficients B_3 and B_4 in terms of ϵ are

$$\begin{aligned} &\sum_{\mathbf{k}_1\mathbf{k}_2}B_3\sim\epsilon\hbar\omega_{\mathbf{k}}\ ,\\ &\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}B_4\sim\epsilon^2\hbar\omega_{\mathbf{k}}\ . \end{aligned} \tag{28}$$

The perturbative approximation of the TGF consistent with the Hamiltonian of Eq. (26) is

$$G_{\mathbf{k}jj'}(i\omega_n)=\delta_{jj'}g^0_{\mathbf{k}j}(i\omega_n)+g^0_{\mathbf{k}j}(i\omega_n)\mathcal{S}_{\mathbf{k}jj'}(i\omega_n)g^0_{\mathbf{k}j}(i\omega_n)+\cdots\ , \tag{29}$$

where $g^0_{\mathbf{k}j}(i\omega_n)$ is the Fourier transform of the harmonic propagator

$$g^0_{\mathbf{k}j}(i\omega_n)=\frac{1}{\beta\hbar}\left[\frac{1}{\omega_{\mathbf{k}j}+i\omega_n}+\frac{1}{\omega_{\mathbf{k}j}-i\omega_n}\right] \tag{30}$$

and $\mathcal{S}_{\mathbf{k}jj'}(i\omega_n)$ is the self-energy matrix (see Appendix A). The lowest-order correction to the spectral density due to the anharmonic terms of the potential may be obtained by keeping only the diagonal terms of the self-energy matrix.[22] This approximation is equivalent to representing the crystal vibrations by a set of noninteracting particles of moment **k** and polarization j, with finite lifetimes and shifted energies. Within this approximation the TGF has the following exact expression:

$$G_{\mathbf{k}j}(i\omega_n)=\frac{2\omega_{\mathbf{k}j}}{\beta\hbar[\omega^2_{\mathbf{k}j}-(i\omega_n)^2]-2\omega_{\mathbf{k}j}\mathcal{S}_{\mathbf{k}jj}(i\omega_n)} . \tag{31}$$

It can be seen from Eqs. (25) and (31) that for frequencies $\omega\simeq\omega_{\mathbf{k}}$ the one-phonon spectral densities are

$$f^1_{\mathbf{k}jj}(\omega)$$
$$=2[n(\omega)+1]\frac{\Gamma_{\mathbf{k}j}(\omega)}{[\omega-\omega_{\mathbf{k}j}-\Delta_{\mathbf{k}j}(\omega)]^2+|\Gamma_{\mathbf{k}j}(\omega)|^2} , \tag{32}$$

$n(\omega)$ being the Bose occupation number at frequency ω. The quantities $\Delta_{\mathbf{k}j}$ and $\Gamma_{\mathbf{k}j}$ are defined as follows:

$$\lim_{v\to 0}\mathcal{S}_{\mathbf{k}jj}(\omega+iv)=-\beta\hbar[\Delta_{\mathbf{k}j}(\omega)-i\Gamma_{\mathbf{k}j}(\omega)] , \tag{33}$$

they coincide with the phonon frequency shifts and bandwidths, respectively, when they are evaluated at frequencies $\omega=\omega_{\mathbf{k}j}$. In the low-frequency limit, $\omega\ll\omega_{\mathbf{k}j}$, the one-phonon spectral densities become

$$f^1_{\mathbf{k}jj}(\omega)=8[n(\omega)+1]\frac{\Gamma_{\mathbf{k}j}(\omega)}{\omega^2_{\mathbf{k}j}} . \tag{34}$$

Here $\Gamma_{\mathbf{k}j}(\omega)$ can be interpreted as the width of the response function at frequency ω.

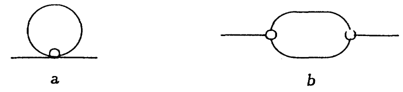

FIG. 1. Lower-order diagrams occurring in the expansion of the phonon self-energy.

As can be seen from Eq. (32) the response function is peaked around harmonic vibrational frequencies. In the limit of a harmonic lattice it would be composed by δ functions centered at the phonon frequencies associated with the first term of Eq. (29). Then the only possibility that energy exchange could occur would be through the lattice transitions with energies corresponding to the NQR frequency (*direct* processes). In molecular crystals the phonons which produce the time variation of the EFG are those involving rotational motions and they have very high frequencies compared with ω_Q. By this reason the *direct* mechanism is negligible, and, as we shall see, the first contribution to W_1 comes from three-phonon processes.

The lower-order contributions (ϵ^2) to the spectral density from the anharmonic terms should be those related with the propagator diagrams like Fig. 1.

It can be shown[16] that only Eq. 1(b) contributes to $\Gamma_{\mathbf{k}j}(\omega)$ in Eq. (34). These terms are associated with the cubic coefficients of the vibrational Hamiltonian, and their contribution to the width of the response function is

$$\begin{aligned}\Gamma_{\mathbf{k}j}(\omega_Q)=\frac{18\pi}{\hbar^2}\sum_{\mathbf{k}_1\mathbf{k}_2}&|B_3(\mathbf{k}\mathbf{k}_1\mathbf{k}_2)|^2\cdot\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k})\\ &\times\{(n_1+n_2+1)[\delta(\omega_1+\omega_2-\omega_Q)-\delta(\omega_1+\omega_2+\omega_Q)]\\ &\quad+(n_1-n_2)[\delta(\omega_1-\omega_2+\omega_Q)-\delta(-\omega_1+\omega_2+\omega_Q)]\} .\end{aligned} \tag{35}$$

Finally, after inserting Eqs. (35) and (34) into Eq. (12), W_1 takes the following expression:

$$\begin{aligned}W_1=\frac{9\pi\omega_Q^2}{\hbar L}\sum_{ss'}\sum_{\mathbf{k}j}&v(s|\mathbf{k}j)v^*(s'|\mathbf{k}j)\omega^{-3}_{\mathbf{k}j}a_s a_{s'}\\ &\times\sum_{\mathbf{k}_1\mathbf{k}_2}|B_3(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k})(n_{\mathbf{k}_1j_1}-n_{\mathbf{k}_2j_2})[n(\omega_Q)+1]\\ &\quad\times[\delta(\omega_{\mathbf{k}_2}-\omega_{\mathbf{k}_1}-\omega_Q)-\delta(\omega_{\mathbf{k}_1}-\omega_{\mathbf{k}_2}-\omega_Q)]+O(\epsilon^4) .\end{aligned} \tag{36}$$

This is a contribution which arises exclusively due to the anharmonicity of the lattice. The thermal bath can dissipate the energy coming from the nuclear spin system at frequency ω_Q by means of the three phonon processes. As can be seen from Eq. (36) this mechanism is driven by the cubic terms of the lattice Hamiltonian. These spin-lattice processes contributing to W_1 are known as *anharmonic Raman* and can be summarized with schemes like Fig. 2 (see, e.g., Ref. 23).

A nuclear quantum is annihilated with a three-phonon process. The dashed line represents a virtual phonon of momentum **k**. This short lifetime excitation of the lattice soon dissipates its energy in a three-phonon collision. The solid lines represent lattice phonons of momentum $\mathbf{k}_1$

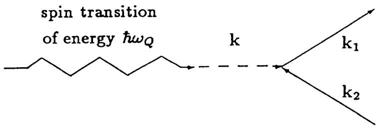

FIG. 2. Diagram representing the spin-phonon mechanisms involved in the anharmonic Raman processes.

and $\mathbf{k}_2$. The intermediate state does not need to conserve energy. The density of these processes is expected to be higher than the direct mechanism because here phonons of all frequencies can participate.

The sum over $\mathbf{k}$ in Eq. (36) includes all values of $\mathbf{k}$ associated to rotational motions of the molecule. As a closed expression for the dispersion relations of the optic phonons is not available, the sum cannot be solved analytically. Generally it can be assumed that eigenvectors and eigenfrequencies are smooth functions of $\mathbf{k}$. The dependence of the B_3 coefficients on $\mathbf{k}$ is determined by the intermolecular anharmonic constants of force. In order to represent all the dynamics by a unique parameter (correlation time), as the semiclassical models do, one should try to perform the sums over $\mathbf{k}_1$ and $\mathbf{k}_2$ independently from the value of $\mathbf{k}$ but this step would be meaningless in the case of anharmonic molecular crystals, because of the $\mathbf{k}$ dependence of B_3 and the momentum-conservation condition. Then, we see that it might not always be right to describe $T_1(T)$ in terms of a unique correlation time of the molecular torsional oscillations.[4,5]

Equation (36) for W_1 explicitly reflects the molecular order in the crystal. Any process capable of altering the molecular order in the lattice could affect this contribution to the spectral density.

The temperature dependence at constant crystalline configuration of W_1 comes mainly from the mean occupation numbers in Eq. (36). At high temperatures $(\hbar\omega_{\mathbf{k}j} \ll k_B T)$

$$(n_{\mathbf{k}_1 j_1} - n_{\mathbf{k}_2 j_2})[n(\omega_Q)+1] \simeq (n_{\mathbf{k}_1 j_1} - n_{\mathbf{k}_2 j_2}) n(\omega_Q)$$

$$\simeq T^2 \frac{4k_B^2}{\hbar^2 \omega_Q} \left[\frac{1}{\omega_{\mathbf{k}_1 j_1}} - \frac{1}{\omega_{\mathbf{k}_2 j_2}} \right] . \tag{37}$$

Therefore, at order ϵ^2, W_1 has a *quadratic* temperature dependence at constant crystalline configuration.

C. Calculation of W_2

In order to obtain W_2 one has to calculate the spectral density of the two-phonon correlation function involved in Eq. (24):

$$f^{(2)}_{\mathbf{k}j\mathbf{k}'j'} \equiv \mathcal{F}\{ \langle A_{\tilde{\mathbf{k}}\tilde{j}}(t) A_{\tilde{\mathbf{k}}'\tilde{j}'}(t) A^*_{\mathbf{k}j} A^*_{\mathbf{k}'j'} \rangle \} . \tag{38}$$

Here we also use the TGF to calculate the two-phonon propagator which is defined as[21]

$$G^{\mathrm{II}}(t) = \langle \mathrm{T}_t A_{\tilde{\mathbf{k}}\tilde{j}}(t) A_{\tilde{\mathbf{k}}'\tilde{j}'}(t) A^*_{\mathbf{k}j} A^*_{\mathbf{k}'j'} U(\beta,0) \rangle_{\mathrm{conec}} . \tag{39}$$

T_t is the time-ordering operator and the subscript conec indicates that only the connected diagrams have to be included in the calculation. The operator $U(\beta,0)$ has the following form:

$$U(\beta,0) = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int_0^{\beta} dt_1 H_{\mathrm{int}}(t_1) \cdots \int_0^{\beta} dt_n H_{\mathrm{int}}(t_n) , \tag{40}$$

where H_{int} symbolizes the anharmonic terms of the vibrational Hamiltonian in the interaction representation. We study the influence of the anharmonicity on W_2 by pointing out the effects that the phonon self-energy has on the two-particle spectral densities. To do this we calculate the lower-order terms of the *renormalized* two-phonon spectral densities and then compare it with the harmonic term.

By making $n=0$ in Eqs. (39) and (40) and using the pairing theorem we obtain

$$\begin{aligned} G^{\mathrm{II}}_{n=0}(t) = {} & \langle \mathrm{T} A_{\tilde{\mathbf{k}}\tilde{j}}(t) A_{\tilde{\mathbf{k}}'\tilde{j}'}(t) \rangle \langle \mathrm{T} A^*_{\mathbf{k}j} A^*_{\mathbf{k}'j'} \rangle \\ & + \langle \mathrm{T} A_{\tilde{\mathbf{k}}\tilde{j}}(t) A^*_{\mathbf{k}j} \rangle \langle \mathrm{T} A_{\tilde{\mathbf{k}}'\tilde{j}'}(t) A^*_{\mathbf{k}'j'} \rangle \\ & + \langle \mathrm{T} A_{\tilde{\mathbf{k}}\tilde{j}}(t) A_{\mathbf{k}'j'} \rangle \langle \mathrm{T} A_{\tilde{\mathbf{k}}'\tilde{j}'}(t) A_{\mathbf{k}j} \rangle . \end{aligned} \tag{41}$$

The first term of the second member in Eq. (41) is an equal-time contribution and corresponds to the stationary part of the spin-lattice Hamiltonian. This term gives no contribution to the spin-lattice relaxation time. The two following terms give equal contributions, therefore we calculate one of them and duplicate the result. Then we have to follow the same steps as in the calculation of W_1: obtaining the discrete Fourier transform of the two-particle propagators, making an analytic prolongation over the whole complex plane and taking the limit for $\nu \to 0$ of the imaginary part of the Green function.

Let us call $G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l)$ to the discrete Fourier transform of the second term of Eq. (41). Starting from the discrete Fourier transform of the one-phonon propagators and using the periodicity of the two-phonon propagators we get

$$G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l) = \sum_{n=-\infty}^{\infty} G_{\mathbf{k}j}(i\omega_n) G_{\mathbf{k}'j'}(i\omega_l - i\omega_n) . \tag{42}$$

Phonon lifetime (anharmonicity) effects can be taken into account by considering the "exact" expression for the one-phonon Green functions. At this step we use the same degree of approximation for the one-phonon Green functions shown in Eq. (29). By replacing Eq. (29) in Eq. (42) and keeping up to the linear terms in $\mathcal{S}$ we find

$$\begin{aligned} G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l) = \sum_n [& \mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l - i\omega_n) + \mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\mathcal{S}_{\mathbf{k}jj}(i\omega_n)\mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l - i\omega_n) \\ & + \mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l - i\omega_n)\mathcal{S}_{\mathbf{k}'j'j'}(i\omega_l - i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l - i\omega_n) + \cdots] \, . \end{aligned} \tag{43}$$

The renormalized two-particle propagator can be represented by a diagram like Fig. 3. The double arrows symbolize the propagation of two particles in a dissipative medium, interacting with the field produced by the other particles. Any correlation among them is neglected.[24] In the two following sections we calculate the spectral densities associated with the two-particle harmonic propagators [called "first-order Raman processes" (Ref. 2)] and with the crossed terms involving the self-energy matrix (hereafter "interaction processes").

1. First-order Raman processes

First we analyze the contribution to W_2 from the first term of Eq. (43):

$$G^{1\text{R}}_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l) = \sum_n \mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l - i\omega_n) \, . \tag{44}$$

This series can be summed by means of contour integrals and the result is[26]

$$G^{1\text{R}}_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l) = \frac{1}{\beta\hbar}\left[\frac{n_{\mathbf{k}} + \mathbf{n}_{\mathbf{k}'} + 1}{\omega_{\mathbf{k}j} + \omega_{\mathbf{k}'j'} + i\omega_l} - \frac{n_{\mathbf{k}} - n_{\mathbf{k}'}}{\omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'} + i\omega_l} + \frac{n_{\mathbf{k}} + n_{\mathbf{k}'} + 1}{\omega_{\mathbf{k}j} + \omega_{\mathbf{k}'j'} - i\omega_l} - \frac{n_{\mathbf{k}'} - n_{\mathbf{k}}}{\omega_{\mathbf{k}'j'} - \omega_{\mathbf{k}j} + i\omega_l} \right] . \tag{45}$$

The harmonic two-phonon spectral density associated to this Green function can be obtained starting from a similar relation than Eq. (25) adapted for two particles. Then, by making use of Eqs. (12) and (24), a straightforward calculation leads to the 1R contribution:

$$\begin{aligned} W_2^{1\text{R}} = \frac{\pi\hbar^2\omega_Q^2}{64L^2} \sum_{\{s\}} \sum_{\mathbf{k}j\mathbf{k}'j'} & v(s|\mathbf{k}j)v(s'|\mathbf{k}j)v(s''|\mathbf{k}'j')v(s'''|\mathbf{k}'j')[1 + n(\omega_Q)](n_{\mathbf{k}} - n_{\mathbf{k}'})(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'})^{-1}a_s a_{s'} a_{s''} a_{s'''} \\ & \times [\delta(\omega_{\mathbf{k}'j'} - \omega_{\mathbf{k}j} - \omega_Q) - \delta(\omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'} - \omega_Q)] \, . \end{aligned} \tag{46}$$

The processes governing this contribution can be represented with diagrams like Fig. 4.

A quantum of energy $\hbar\omega_Q$ from a nuclear spin transition of $\Delta m = \pm 2$ is annihilated in a two-phonon process which creates a phonon of frequency $\omega_{\mathbf{k}j}$ and destroys a phonon of frequency $\omega_{\mathbf{k}'j'}$. The frequencies must verify the relation $\omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'} = \pm\omega_Q$. Unlike W_1 no virtual phonon states are present here; this is a completely harmonic mechanism.

As for W_1, the temperature dependence at a constant crystalline configuration of $W_2^{1\text{R}}$ is quadratic within the high-temperature range. But in this case the relaxation is driven by harmonic fluctuations. The energy exchange between the nuclear spin system and the lattice is resonant. The relevance of these energy exchange processes is determined by the two-phonon density of states.

Generally it can be assumed that both the eigenvectors and eigenfrequencies in Eq. (46) are smooth functions of the wave vector. Then it would be possible to average the $\mathbf{k}$ dependence of $W_2^{1\text{R}}$ over the entire reciprocal space. Besides, if the low-frequency torsional motions are those giving the main contribution to $W_2^{1\text{R}}$ then we can write

$$W_2^{1\text{R}} = \frac{\pi}{16}(\hbar\omega_Q)^2 \sum_s \left[\frac{a_s^2}{\omega_s} \right]^2 [1 + n(\omega_Q)]\tau^{1\text{R}} \, , \tag{47}$$

where we defined the quantity $\tau^{1\text{R}}$, having units of time, as

$$\begin{aligned} \tau^{1\text{R}} = \sum_{\mathbf{k}j\mathbf{k}'j'} (n_{\mathbf{k}} - n_{\mathbf{k}'}) [& \delta(\omega_{\mathbf{k}'j'} - \omega_{\mathbf{k}j} - \omega_Q) \\ & - \delta(\omega_{\mathbf{k}j} - \omega_{\mathbf{k}'j'} - \omega_Q)] \, . \end{aligned} \tag{48}$$

Consequently, it is possible to describe the contribution to the spin-lattice relaxation from the 1R processes in terms of a single characteristic time, representing the

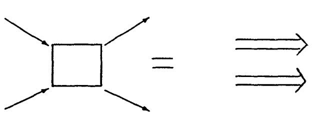

FIG. 3. Renormalized two-phonon propagator expansion (see text).

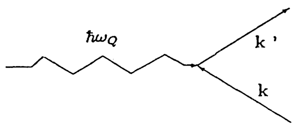

FIG. 4. Diagram representing the first-order Raman spin-phonon processes. No virtual phonons are involved.

harmonic fluctuations of the lattice. Naturally, this result coincides with the semiclassical model,[4,5] where the spin-lattice relaxation is described through a stochastic process representing all the fluctuations of the crystalline mean field. The relative value of W_1 and $W_2^{1\mathrm{R}}$ depends on the value that $\tau^{1\mathrm{R}}$ takes. Except in the cases where the transition probabilities can be measured separately, it is not possible to know which of these mechanisms is dominant. As we will show elsewhere, it would be possible to get some knowledge about the relative importance of the collective processes through uniaxial stress experiments.

2. *Interaction processes*

Up to now the study of the nuclear spin-lattice relaxation in molecular crystals in terms of vibrational fluctuations by making a quantum approach for describing the lattice allowed us to realize that nuclear transitions with $\Delta m = \pm 1$ and $\Delta m = \pm 2$ are coupled with different kinds of processes which could be of similar magnitude. Both AR and 1R processes give a quadratic temperature dependence in an intermediate-temperature range. This dependence is similar to that found in Ref. 2. In that work higher-order contributions due to the phonon self-energy effects over the two-particle spectral densities were neglected. However such terms would represent a sort of interaction between the two processes described above and this mechanism could become significant for molecular crystals as we show. Let us call this kind of relaxation mechanism *interaction processes.* This contribution represents the first-order correction to the harmonic two-particle propagator due to phonon self-energy.

Now we analyze the contribution coming from the cross products of Eq. (43) following a procedure similar to that employed in obtaining the former contributions. As we have seen above, two terms, Figs. 1(a) and 1(b), contribute in $O(\epsilon^2)$ to the self-energy matrix. Figure 1(a) is related to the quartic terms of the vibrational Hamiltonian and does not contribute to the excitation lifetime, giving no correction to the two-particle spectral densities. On the other hand, Fig. 1(b) is related to the cubic coefficients of the crystal Hamiltonian and gives the next nonzero contribution to the spectral density. This term is of $O(\epsilon^2)$ relative to $W^{1\mathrm{R}}$. Some aspects of this calculus are depicted in Appendix A.

The obtained result for the transition rate associated to the interaction mechanism, W_2^{int}, in the limit of high temperature is

$$
\begin{aligned}
W_2^{\mathrm{int}} = \frac{9\pi\omega_Q^3}{32L^2} k_B T \sum_{\{s\}} \sum_{\mathbf{k}j\mathbf{k}'j'} & v(s|\mathbf{k}j)v(s'|\mathbf{k}j)v(s''|\mathbf{k}'j')v(s'''|\mathbf{k}'j')[1+n(\omega_Q)]a_{\{s\}} \\
& \times \sum_{\mathbf{k}_1\mathbf{k}_2} |B_3(\mathbf{k}'j',\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2 \Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}')(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'})^{-1} \\
& \times \left\{ \delta(\omega_{\mathbf{k}'}-\omega_{\mathbf{k}}\pm\omega_Q) \left[\frac{n_{\mathbf{k}_1}+n_{\mathbf{k}_2}+1}{2\omega_{\mathbf{k}'}^3(W-\omega_{\mathbf{k}'})_P} + \frac{n_{\mathbf{k}_1}-n_{\mathbf{k}_2}}{2\omega_{\mathbf{k}}^3} \left[\frac{1}{M-\omega_{\mathbf{k}'}} + \frac{1}{M+\omega_{\mathbf{k}'}} \right]_P \right] \right. \\
& \quad + \delta(W-\omega_{\mathbf{k}}\pm\omega_Q) \frac{(n_{\mathbf{k}_1}+n_{\mathbf{k}_2}+1)}{\omega_{\mathbf{k}}^2(\omega_{\mathbf{k}'}+W)(\omega_{\mathbf{k}'}-W)_P} \\
& \quad \left. + [\delta(M-\omega_{\mathbf{k}}\pm\omega_Q)-\delta(M+\omega_{\mathbf{k}}\pm\omega_Q)] \frac{(n_{\mathbf{k}_1}-n_{\mathbf{k}_2})}{\omega_{\mathbf{k}}^2(\omega_{\mathbf{k}'}+M)(\omega_{\mathbf{k}'}-M)_P} \right\} ,
\end{aligned}
\tag{49}
$$

where $M \equiv \omega_{\mathbf{k}_2} - \omega_{\mathbf{k}_1}$, $W \equiv \omega_{\mathbf{k}_2} + \omega_{\mathbf{k}_1}$, and $\delta(a \pm b) = \delta(a+b) + \delta(a-b)$. The subscript P means taking the principal part.

The integration over $\mathbf{k}$ selects the phonons with nonzero projection over the rotational motions and subject to momentum and energy conservation for each fixed value of $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}'$. The resulting functions of $\omega_{\mathbf{k}'}$ present poles at $\omega_{\mathbf{k}'} = \pm W, \pm M$ allowing the possibility of W_2^{int} to take an appreciable value when the integration over $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}'$ is carried out. While developing the last equation we neglected terms proportional to $[2\omega_{\mathbf{k}'}^3(W+\omega_{\mathbf{k}'})]^{-1}$. They are small compared with the others shown in Eq. (49), since their denominators always take large values. As can be seen in Eq. (49) the spectral density associated with this mechanism may increase to some extent due to the great number of phonons that can participate in the interaction mechanism. The phonons labeled with $\mathbf{k}_1, \mathbf{k}_2$ only have to satisfy conservation of energy and momentum, so the restriction of having a rotational character is released. Therefore, the density of states accessible to the nuclear spin relaxation may become markedly increased by this kind of mechanism. The processes contributing to W_2^{int} can be represented by diagrams like Fig. 5.

As in the AR process, here the dashed lines represent virtual phonons. It can be interpreted as if one of the two phonons of the 1R mechanism is now provided by a three-phonon collision that is driven by the cubic terms

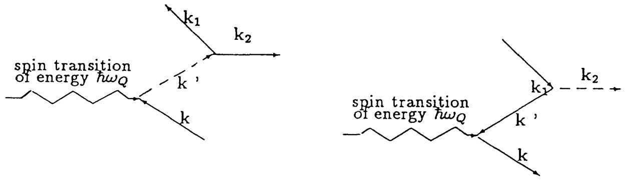

FIG. 5. Diagrams which depict the *interaction* mechanisms associated with the T^3 terms of Eq. (49).

of the vibrational Hamiltonian. This means that the anharmonic fluctuations could enhance the intensity of the spin-lattice coupling provided by the 1R processes, subject to the degree of anharmonicity and the symmetry of the lattice.

It can be seen from Eq. (49) that W_2^{int}, being of $O(\epsilon^2 T)$ relative to $W_2^{1\text{R}}$, has a cubic temperature dependence in the high-temperature regime. Then the temperature dependence of T_1 at constant crystalline configuration can be summarized as

$$T_1^{-1}(T) = AT^2 + BT^3 , \tag{50}$$

where the quadratic term contains the 1R and AR processes and the cubic one arises from the interaction of those mechanisms.

At a rough estimation, $\epsilon^2 T \sim 0.3$ at room temperature. Therefore, the cubic mechanism could become evident as a departure of T_1 data from the usual law $T_1 \propto T^{-2}$. Furthermore, the cubic term could become the leading contribution whenever the density of the interaction processes are large enough. It can be seen from Eq. (50) that even if B is 2 orders of magnitude less than A, a plot of $\ln T_1$ vs $\ln T$ is still a straight line of slope three.

The law $T_1 \propto T^{-2}$ verifies in most monoatomic-like crystals. Van Kranendonk and Walker explained this quadratic behavior with the 1R and AR processes. They neglected the contributions coming from the self-energy effects on the quadratic terms in the local field arguing the smallness of the spin-lattice coupling.[2] However, spin-lattice relaxation in molecular crystals usually show a different behavior. By analyzing Eq. (49) we see that the density of the four-phonon processes depends on the number of phonons $\mathbf{k}_1$ and $\mathbf{k}_2$ satisfying $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}$, where $\mathbf{k}$ stands for rotational phonons giving nonzero values of $B_3(\mathbf{k}j, \mathbf{k}_1 j_1, \mathbf{k}_2 j_2)$. If the anharmonic intermolecular interactions were nearly independent of the position, the cubic term $B_3(\mathbf{k}j, \mathbf{k}_1 j_1, \mathbf{k}_2 j_2)$ would take small values for large $\mathbf{k}$. In such case, the integration domain over $\mathbf{k}$ and $\mathbf{k}'$ in Eq. (49) would be restricted for small $\mathbf{k}$ and $\mathbf{k}'$, excluding phonon processes where $\mathbf{k}_1 + \mathbf{k}_2 \neq 0$. This could be the case of the monoatomic-like ionic crystals where the resonant nucleus "sees" a large number of neighboring atoms placed around with a rather isotropic distribution, interacting with long-range potentials. In contrast, in molecular crystals the atomic distribution is markedly anisotropic and the interactions are of shorter range. A combination of anharmonicity and anisotropy might enhance the importance of the term W_2^{int}, and a contribution like this one could account for the departures from the square temperature law, frequently observed in molecular crystals.

Summarizing, we have calculated the temperature dependence of the transition probabilities *at constant crystalline configuration.* Due to thermal expansion both A and B in Eq. (50) depend indirectly on temperature through their dependence on the eigenfrequencies and the constants of force. In some cases where significant thermal expansion occurs, coefficients A and B could become strongly temperature dependent; enhancing the $T_1(T)$ rate for increasing temperatures (see, for example, ^{35}Cl NQR experiments on chloracetamide in Ref. 25). This fact could be another "ingredient," besides essential anharmonicity, to be considered whenever deviations from the quadratic T_1 dependence become apparent for increasing temperatures.

D. The case of $\eta \neq 0$

In order to explore about the influence of the asymmetry of the EFG tensor on T_1 we have to inquire basically on two points. In the first place it is necessary to estimate the importance of the corrections on W_1 and W_2 that the inclusion of $\eta \neq 0$ implies. Second, we have to analyze the nature of those corrections, namely if they bring some mixing among the various lattice mechanisms which are present in W_1 and W_2 for $\eta = 0$.

This section is concerned with the terms of Eq. (13) involving η and η^2. The typical structure of such terms is

$$\eta[\langle D_{0j}[\Omega(t)] D^*_{\pm 2,j}(\Omega)\rangle + \langle D_{\pm 2,j}[\Omega(t)] D^*_{0j}(\Omega)\rangle] \tag{51}$$

and

$$\eta^2 \langle D_{\pm 2,j}[\Omega(t)] D_{\pm 2,j}(\Omega)^* \rangle \tag{52}$$

for $j = 1,2$.

By inserting the definition of the Wigner matrices of Eq. (5) in the last expressions, and expanding them in the Euler angles to the same order as done in Eqs. (17) and (18), one finds that the lower-order corrections to K_1 and K_2 due to the asymmetry of the EFG contain factors like $\langle q_s(t) q^*_{s'} \rangle$ for $\Delta m = 1$ and like $\langle q_s(t) q_{s'}(t) q^*_{s''} q^*_{s'''} \rangle$ for $\Delta m = 2$. Other terms of the form

$$\sum_{\{s\}} a_s a_{s'} a_{s''} a_{s'''} \langle q_s(t) q^*_{s'} q^*_{s''} q^*_{s'''} \rangle$$

also appear both in K_1 and K_2. The spectral density of a correlation function like this one can be neglected, as described in Appendix B. We can conclude that the inclusion of $\eta \neq 0$ *does not* produce any kind of mixing between processes related with W_1 and those related with W_2 nor introduces new relaxation processes.

III. CONCLUDING REMARKS

In this work we have investigated the consequences of introducing the crystalline nature into the description of the nuclear quadrupole spin-lattice relaxation in molecular crystals. We can conclude that even if the fluctuations of the nuclear quadrupole Hamiltonian can be ascribed only to the molecular motions, it is the *dynamics* of the motions, imposed by the crystal as a whole, which defines the nature of the spin-lattice coupling mechanisms.

We described spin-lattice relaxation in terms of two essentially different and often competing mechanisms: the pseudoharmonic and the anharmonic processes. The first involve the nuclear transitions that are *directly* coupled with harmonic two-phonon transition of the thermal bath in a resonant process. In this kind of process the molecule can be thought as an individual entity immersed in a phonon thermal bath and its dynamics can be described by stochastic processes. In contrast, for describing the anharmonic process it is not possible to keep the picture of individual molecules and collective processes must be included into the description. Therefore, in a general case, it is not meaningful to represent the molecular dynamics with a single parameter like the mean lifetime of the torsional oscillations, as is done in semiclassical models.

The anharmonic intermolecular interactions take part explicitly in the transition rates W_1 and W_2^{int} through the B_3 coefficients [see Eqs. (36) and (49)]. Then the symmetry of the molecule environment plays an important role in the anharmonic contributions to T_1 because the cubic coefficients of the vibrational Hamiltonian reflect explicitly the anisotropy of the crystalline potential. Therefore, any process altering the molecular ordering could affect these contributions. On the contrary, the influence of the crystalline order on the first-order Raman processes comes indirectly through the eigenfrequencies and the correlation time, as can be seen in Eq. (47).

By using a perturbative approach we identified the various contributions to the nuclear spin-lattice relaxation time by their relative magnitude and temperature dependence. A quadratic temperature dependence of T_1^{-1} arises due to 1R and AR processes. As these processes cannot be measured separately in $T_1(T)$ experiments, further experimental information would be necessary to know if one of these mechanisms is dominant. Finally, a third contribution, which we called the *interaction* process, has shown a cubic temperature dependence, being of order $O(\epsilon^2 T)$ relative to the contribution due to 1R processes. This mechanism could become dominant subject to the anharmonicity and particular symmetry of the molecular environment. Contributions like this one could also account for the departure from the T^{-2} law, often observed in molecular crystals.

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APPENDIX A

We analyze here the contribution to the interaction mechanism coming from linear terms in the self-energy in Eq. (43). The terms of our interest involve products of three harmonic propagators and the self-energy like

$$X_1(\omega)=\sum_n \mathbf{g}^0_{\mathbf{k}j}(i\omega_n)\cdot\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l-i\omega_n)\mathcal{S}_{\mathbf{k}'j'j'}(i\omega_l-i\omega_n)\mathbf{g}^0_{\mathbf{k}'j'}(i\omega_l-i\omega_n)\ . \tag{A1}$$

The other term, X_2, has the same structure but exchanging both the arguments of the functions and the indexes **k** and **k**′.

The self-energy of the last expression comes from Fig. 1(b). It has the following form:[16]

$$\mathcal{S}_{\mathbf{k}jj}(i\omega_n)=\frac{18\beta}{\hbar}\sum_{\mathbf{k}_1\mathbf{k}_2}|B_3(\mathbf{k},\mathbf{k}_1,\mathbf{k}_2)|^2\left[N_A\left[\frac{1}{\omega_{\mathbf{k}_1}+\omega_{\mathbf{k}_2}+i\omega_n}+\frac{1}{\omega_{\mathbf{k}_1}+\omega_{\mathbf{k}_2}-i\omega_n}\right]\right.$$
$$\left.+N_B\left[\frac{1}{\omega_{\mathbf{k}_1}-\omega_{\mathbf{k}_2}+i\omega_n}+\frac{1}{\omega_{\mathbf{k}_1}-\omega_{\mathbf{k}_2}-i\omega_n}\right]\right] \tag{A2}$$

with $N_A\equiv n_{\mathbf{k}_1}+n_{\mathbf{k}_2}+1$ and $N_B\equiv n_{\mathbf{k}_1}-n_{\mathbf{k}_2}$. Let us write the contribution to X_1 arising from the term of the self-energy that multiplies N_B:

$$\sum_{\mathbf{k}_1\mathbf{k}_2}N_B F_{\mathbf{k}_1\mathbf{k}_2}(\mathbf{k}',\mathbf{k})\sum_n\left[\frac{1}{\omega_{\mathbf{k}}+i\omega_n}+\frac{1}{\omega_{\mathbf{k}}-i\omega_n}\right]\left[\frac{1}{\omega_{\mathbf{k}'}+i\omega_l-i\omega_n}+\frac{1}{\omega_{\mathbf{k}'}-i\omega_l+i\omega_n}\right]^2$$
$$\times\left[\frac{1}{\omega_{\mathbf{k}_2}-\omega_{\mathbf{k}_1}+i\omega_n-i\omega_l}+\frac{1}{\omega_{\mathbf{k}_2}-\omega_{\mathbf{k}_1}-i\omega_n+i\omega_l}\right]\ , \tag{A3}$$

where we defined the function F as

$$F_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{k}',\mathbf{k})=\sum_{\{s\}}\frac{27}{2}\omega_Q^2\frac{\beta}{\hbar}\left[\frac{\hbar}{2L}\right]^2 v(s|\mathbf{k}j)v(s'|\mathbf{k}j)v(s''|\mathbf{k}'j')v(s'''|\mathbf{k}'j')|B_3(\mathbf{k}',\mathbf{k}_1,\mathbf{k}_2)|^2(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'})^{-1}a_s a_{s'}a_{s''}a_{s'''}\ . \tag{A4}$$

In expressions like Eq. (A3), the sum over index n can be evaluated by contour integration in the complex plane: any function $f(z)$ having poles at $z=i\omega_p\neq i\omega_n$ satisfies

$$\sum_{n} f(i\omega_n)=\beta\hbar\sum_{p}(e^{\beta\hbar i\omega_p}-1)^{-1}R_p(i\omega_p)\ , \tag{A5}$$

where $R_p(i\omega_p)$ is the residue of the function $f(i\omega)$ at the pole ω_p.

The desired spectral density is obtained by analytic prolongation of functions like $X_1(\omega)$ over the complex plane and taking the limit for real values of the frequency, as suggested in Eq. (25). It can be seen that all terms including second-order poles give a null contribution when the limit for $\nu\rightarrow 0$ is taken. Therefore, we exclude products with two equal factors.

In order to illustrate the procedure we calculate the contribution to W_2^{int} from a representative term of Eq. (A3):

$$\widetilde{X}_1=\sum_{\mathbf{k}\mathbf{k}'}\sum_{\mathbf{k}_1\mathbf{k}_2}N_B F'_{\mathbf{k}_1\mathbf{k}_2}(\mathbf{k}',\mathbf{k})\sum_{n}\left[\frac{1}{\omega_{\mathbf{k}}+i\omega_n}\frac{1}{\omega_{\mathbf{k}'}+i\omega_l-i\omega_n}\frac{1}{\omega_{\mathbf{k}'}-i\omega_l+i\omega_n}\frac{1}{M+i\omega_l-i\omega_n}\right]\ , \tag{A6}$$

with M as defined in Eq. (49). After the procedure described above, and using the representation for the Dirac delta: $\lim_{\epsilon\rightarrow 0}[\epsilon/(\epsilon^2+x^2)]=\delta(x)$, the last equation gives

$$\widetilde{X}_1=\sum_{\mathbf{k}_1\mathbf{k}_2}N_B F'_{\mathbf{k}_1\mathbf{k}_2}(k',k)\left\{\Phi(-\mathbf{k})\left[\frac{\delta(\omega_{\mathbf{k}'}-\omega_{\mathbf{k}}-\omega_Q)}{(\omega_{\mathbf{k}'}+\omega_{\mathbf{k}}+\omega_Q)(M+\omega_{\mathbf{k}}+\omega_Q)}-\frac{\delta(M+\omega_{\mathbf{k}}+\omega_Q)}{(\omega_{\mathbf{k}'}+\omega_{\mathbf{k}}+\omega_Q)(\omega_{\mathbf{k}'}-\omega_{\mathbf{k}}-\omega_Q)}\right]\right.$$
$$\left.-\Phi(-\mathbf{k}')\left[\frac{\delta(\omega_{\mathbf{k}'}-\omega_{\mathbf{k}}-\omega_Q)}{(2\omega_{\mathbf{k}'})(M+\omega_{\mathbf{k}'})}\right]\Phi(M)\left[\frac{\delta(M+\omega_{\mathbf{k}}+\omega_Q)}{(\omega_{\mathbf{k}'}-M)(\omega_{\mathbf{k}'}+M)}\right]\right\}\ , \tag{A7}$$

where

$$\Phi(\mathbf{k})\equiv(e^{\beta\hbar i\omega_{\mathbf{k}}}-1)^{-1}\ .$$

It is worth remarking that $\omega_{\mathbf{k}}$ and $\omega_{\mathbf{k}'}$ are the frequencies of vibrational modes having nonzero projection on the rotational motions, their value is about 10^{13} Hz for all $\mathbf{k}$, while $\omega_{\mathbf{k}_1}$ and $\omega_{\mathbf{k}_2}$ have no restriction. The resonance frequencies, ω_Q, are usually between tens and hundreds of megahertz, therefore $\omega_Q\ll\omega_{\mathbf{k}}$. Consequently, any term having $\delta(\omega_{\mathbf{k}'}+\omega_{\mathbf{k}}\pm\omega_Q)$ does not contribute to the result. When calculating all terms of X_1 and X_2, some of them cancel for the same reason.

When replacing all the terms having the structure of Eq. (A7) into Eq. (A3), one obtains factors like

$$\coth\left[\frac{\beta\hbar M}{2}\right]-\coth\left[\frac{\beta\hbar(M-\omega_Q)}{2}\right]$$

after expanding this difference to the first order in ω_Q we notice that it is of order:

$$-\frac{2\omega_Q}{\omega_{\mathbf{k}}}\frac{k_B T}{\hbar\omega_{\mathbf{k}}}$$

and it gives the explicit linear temperature dependence arising in Eq. (49).

All terms contributing to W_2^{int} have vanishing denominators. The density of these integrable poles depends on the dispersion relations. Then, the relative importance of this contribution to the relaxation rate relies on the particular features of this distribution in each crystal.

APPENDIX B

In this appendix we estimate the contribution of the term $\widetilde{k}_1$ of Eq. (20) to the correlation function K_1. In terms of the phonon operators it is

$$\widetilde{k}_1=\left[\frac{\hbar}{2L}\right]^2\sum_{\{s\}}\sum_{\mathbf{k}j,\mathbf{k}'j'}v(s|\widetilde{\mathbf{k}}\widetilde{j})v^*(s'|\widetilde{\mathbf{k}}'\widetilde{j}')v^*(s''|\mathbf{k}j)v^*(s'''|\mathbf{k}'j')a_s a_{s'}a_{s''}a_{s'''}\langle A_{\widetilde{\mathbf{k}}\widetilde{j}}(t)A^*_{\widetilde{\mathbf{k}}'\widetilde{j}'}A^*_{\mathbf{k}j}A^*_{\mathbf{k}'j'}\rangle(\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}\omega_{\widetilde{\mathbf{k}}\widetilde{j}}\omega_{\widetilde{\mathbf{k}}'\widetilde{j}'})^{-1/2}\ . \tag{B1}$$

First we concentrate on the correlation function which involves four phonon operators. It has the same structure of Eq. (39) but in this case one operator is evaluated at time t and the other three at $t=0$. By using the pairing theorem we get

$$G^{\text{II}}_{n=0}(t)=3\langle \mathrm{T}A_{\widetilde{\mathbf{k}}\widetilde{j}}(t)A^*_{\widetilde{\mathbf{k}}'\widetilde{j}'}\rangle\langle \mathrm{T}A^*_{\mathbf{k}j}A^*_{\mathbf{k}'j'}\rangle \tag{B2}$$

and then follow the same steps of the calculus of $W_2^{1\text{R}}$. In order to get the discrete Fourier transform of Eq. (B2), we repeat the procedure that leads to Eq. (42). The equivalent equation takes the form

$$G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l)=G_{\mathbf{k}j}(i\omega_l)\sum_{n=-\infty}^{\infty}G_{\mathbf{k}'j'}(i\omega_n)\ . \tag{B3}$$

Again $G_{\mathbf{k}j}(i\omega_n)$ are the "exact" one-phonon propagators. Notice that Eq. (B3) is similar but not equal to Eq. (42).

By including the lower-order corrections to the harmonic propagators:

$$G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l)=G_{\mathbf{k}}(i\omega_l)\sum_m g^0_{\mathbf{k}'}(i\omega_m)+g^0_{\mathbf{k}j}(i\omega_l)\sum_n g^0_{\mathbf{k}'j'}(i\omega_n)\mathcal{S}_{\mathbf{k}'}(i\omega_n)g^0_{\mathbf{k}'j'}(i\omega_n)+\cdots \ . \tag{B4}$$

Using the definition of the harmonic propagators in Eq. (30) and the self-energy matrix from Eq. (A3) it can be seen that the second term of the last equation, in the limit of $\nu \rightarrow 0$ (real frequencies), is proportional to δ functions like $\delta(\omega_{\mathbf{k}}-\omega_Q)$. Then this term does not contribute to Eq. (20) because the condition $\omega_{\mathbf{k}}=\omega_Q$ can never be fulfilled. On the other hand, the first term of Eq. (B4) gives[16]

$$G_{\mathbf{k}j\mathbf{k}'j'}(i\omega_l)=G_{\mathbf{k}}(i\omega_l)(2n_{\mathbf{k}'}+1) \ . \tag{B5}$$

Then let us estimate the magnitude of the spectral density of Eq. (B1)

$$\tilde{\mathcal{J}}_1=\left[\frac{\hbar}{2L}\right]^2\sum_{\{s\}}\sum_{\mathbf{k}j,\mathbf{k}'j'} v(s|\mathbf{k}j)v^*(s'|\mathbf{k}'j')v^*(s''|\mathbf{k}j)v^*(s'''|\mathbf{k}'j')a_s a_{s'} a_{s''} a_{s'''} 8\Gamma_{\mathbf{k}}(\omega)[n(\omega)+1](2n_{\mathbf{k}'}+1)/\omega_{\mathbf{k}}^2 \ . \tag{B6}$$

By using the definition of $\Gamma_{\mathbf{k}}(\omega)$ and realizing that the sum over $\mathbf{k}'$ is independent of the index $\mathbf{k}$, it is possible to relate this contribution to W_1^{AR}:

$$\tilde{\mathcal{J}}_1=\frac{\hbar}{2L}\sum_{\{s\}}\sum_{\mathbf{k}'j'} v^*(s''|\mathbf{k}'j')v^*(s'''|\mathbf{k}'j')a_{s''}a_{s'''}\coth(\hbar\omega_{\mathbf{k}'}/2k_B T)W_1^{\mathrm{AR}} \ , \tag{B7}$$

where

$$\coth(\hbar\omega_{\mathbf{k}'}/2k_B T)\simeq(2k_B T/\hbar\omega_{\mathbf{k}'})\simeq 4$$

and

$$(\hbar a_{s''}a_{s'''}/\omega_{\mathbf{k}'})\simeq 10^{-3} \ .$$

Therefore, this term is of the order of one-hundredth of W_1^{AR} or less. Its temperature dependence is cubic, but it is small compared with the contribution calculated in Eq. (36).

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