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Nuclear quadrupolar spin-lattice relaxation with realistic phonon density of states in alkali halides

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The nuclear quadrupolar spin-lattice relaxation times T_1 have been calculated in alkali halides, whereby the phonon density of states have been extracted from the shell model lattice dynamics. The calculations at room temperature were performed on ^{79}Br in KBr, NaBr, and RbBr; ^{23}Na in NaI, NaCl, and NaBr; ^{35}Cl in NaCl and KCl; and ^{127}I in NaI and KI. The obtained values of relaxation time T_1 are an order of magnitude smaller than those calculated with the Debye-model phonon density of states and agree well with experiments. The temperature dependence of acoustic and optical phonon contributions to the nuclear relaxation rate (first-order Raman phonon process) are carried out in the temperature range 20 to 300 K for ^{23}Na and ^{127}I in NaI. The role of optical phonons becomes important from 77 K on; the temperature dependence of T_1 agrees with experimental data throughout most of the temperature range studied (77-300 K), while differing quantitatively from the predictions obtained on the basis of the Debye-model.

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I. INTRODUCTION

The nuclear spin-lattice relaxation (SLR) in crystals, which originates from interaction between nuclear spin system and lattice thermal vibrations, does essentially depend on the temperature and phonon density of states (PDOS). In this work, the sensitivity of SLR time T_1 to the particularities of PDOS in several alkali halides is studied, with a special aim to estimate the relative contributions of acoustic and optical phonons. For a typical alkali halide crystal NaI, the variation of T_1 with temperature ranging from 20 to 300 K is investigated to derive the correlation with the form and nature of PDOS.

The quadrupolar nuclear SLR in ionic crystals has been widely studied both theoretically and experimentally starting from the 1950 paper by Pound [1] and further on into the late 1960s. However, since the Van Kranendonk's (VK) celebrated paper [2] of 1954 on the theory of quadrupolar nuclear spin-lattice relaxation, we are not aware of any attempts to construct a quantitative theory for ionic crystals. Other theoretical models were proposed at around that time by Japanese physicists: the Yosida and Moriya covalent model [3] was based on variations of covalent bonding arising from phonons, whereas the Kanda and Yamashita overlap model [4] considered the overlap covalency originating from the "exchange effect". Neither model was further developed. However, complimentary modifications have been made to the VK theory to validate the experimental results of SLR time, which came out unexpectedly short. In the following, we cite the main modifications. First, Wikner, Blumberg and Hahn [5] considered the induced dipole mechanism, while Kochelaev [6] incorporated an approximate distribution function for the optical phonons into the VK treatment. Second, in their original work [7], Joshi, Gupta, and Das used the phonon spectrum calculated on the basis of the Born lattice theory, rather than the model Debye function. Ray and Sangster [8] calculated T_1 on the basis of Breathing shell model using a Green's function formalism in NaI crystal, and Pietilä [9] applied a rigid shell model for lattice vibrations to determine the anharmonic SLR in NaCl.

The present work was motivated essentially by a recent progress in phonon calculations provided by modern atomistic simulation of solids using computer codes (GULP, Wien2k, CASTEP). The calculation of the heat capacities of solids as a thermodynamic function from PDOS using computer programs became a common task for materials scientists. An extension over extracting the SLR time, an informative thermodynamic function of the

crystal lattice, accurately available from PDOS, seems desirable and feasible. Such calculations were carried out recently for electronic spin-lattice relaxation [10]. Thurber and Tycko [11] demonstrated the use of SLR time T_1 of ^{79}Br nuclei in KBr as a temperature-dependent parameter enabling to probe the internal sample temperature. Beckett *et al.* [12] also considered KBr as an effective internal temperature calibrant for cryogenic nuclear magnetic resonance (NMR). Other alkali halides have been investigated [13] with similar goals. The determination of sample temperature in the rapidly spinning rotor of modern NMR spectrometer remains a technically difficult problem to solve. We think that such SLR investigations can contribute to finding an efficient solution.

The paper is organized as follows. Sec. II outlines the theoretical method for the T_1 calculation based on the VK – Walker expressions [14] and PDOS obtained from lattice quasi-harmonic dynamics. The derived formula and the PDOS curves from a computer code, GULP [16], are used in Sec. III to calculate the values of T_1 in several alkali halides as well as the temperature dependence of relaxation time for ^{23}Na and ^{127}I in NaI. The conclusion is presented in Sec. IV.

II. METHOD

A. Lattice Dynamics

The lattice dynamics calculations of vibrational properties employed here are based on the simple ionic shell model [15]. In this model the crystal is conceived as an assembly of point charges interacting via Coulomb and short-range potential functions. For alkali halide crystals, it is widely accepted to describe the short-range interaction with a pairwise Buckingham potential:

$$\phi = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}, \quad (1)$$

where the parameters A , ρ and C are usually determined by semi-empirical or *ab initio* methods; r is the inter-ionic distance. With the dynamical matrix $\mathbf{D}$ constructed in reciprocal space, the angular phonon frequencies $\omega_{\vec{k},s}$ (where $\vec{k}$ is the phonon wave vector and s is a mode index) can be found from the standard eigenvalue equation:

$$\omega_{\vec{k},s}^2 \vec{e}_s(\vec{k}) = \mathbf{D}(\vec{k}) \vec{e}_s(\vec{k}), \quad (2)$$

where $\vec{e}_s$ is the polarization vector. To solve Eq. (2), the dynamical matrix $\mathbf{D}$ must be diagonalized in the first Brillouin zone (1BZ). Having obtained the phonon frequencies $\nu_i = 2\pi/\omega_{\vec{k},s}$ for every $\vec{k}$ and every mode s , one can extract the phonon dispersion curves (PDC) and the phonon density of states $G(\nu)$.

All calculations were performed using the computer code GULP [16] incorporating quasi-harmonic lattice dynamics. The quasi-harmonic approximation is necessary for calculating PDOS at finite temperatures, which is otherwise difficult to do with other more sophisticated *ab initio* codes.

Parameters of the Buckingham potential are downloaded from the CATLOW internet library [17]; the core – shell cut-off distance was set to 12 Å throughout this work. In order to perform the PDOS integration in reciprocal space, GULP [16] uses a standard scheme of Monkhorst and Pack [18] for choosing the grid points. The shrinking factors used in our work for 1BZ summation were taken as 150 for each reciprocal lattice vector.

B. T_1 calculation

In this work we consider that the main contribution to the relaxation time T_1 is coming from the first-order Raman process (1R), also known as the monopole one. This process arises from the coupling between the nuclear quadrupole moment and the quadratic part of electric field gradient expansion in power series with respect to the nuclear displacements.

VK and Walker (1968) established an elegant formula for the transition probability of 1R process [14]. The probability of NMR transitions from states m to states $m \pm 1, \pm 2$ accompanied by the creation of one phonon and the annihilation of another to conserve energy is given by

$$W_{1R} = 16\pi\kappa \sum_{m=1}^2 m^2 \sum_{\lambda_1, \lambda_2} \left| f_{\lambda_1, \lambda_2}^{(m)} \right|^2 \times n_1(n_2 + 1) \delta(\varepsilon_{\lambda_2} - \varepsilon_{\lambda_1} - m\varepsilon_0), \quad (3)$$

where

$$\kappa = \frac{3(eQ)^2(2I + 3)}{10\hbar(2I)^2(2I - 1)}. \quad (4)$$

The spin-lattice coupling constants $f_{\lambda_1, \lambda_2}^{(m)}$ can be approximately defined in the framework of the point-charge model for NaCl-type crystals as [14]

$$f_{\lambda_1, \lambda_2}^{(m)} \approx d_m \xi_{k_1} \xi_{k_2}, \quad \text{with} \quad \xi_k = \sqrt{\frac{\hbar k}{2NMv_D}}, \quad (5)$$

where N is the number of unit cells, M is the atomic mass and v_D is the Debye sound velocity, k is the wave number. The coefficients d_m in (5) may be expressed through microscopic parameters as follows [2]:

$$d_1 = 1.56 \left(\frac{\gamma e}{a^3} \right), \quad d_2 = 1.81 \left(\frac{\gamma e}{a^3} \right), \quad (6)$$

where e is the charge on each neighbour, γ is the anti-shielding Sternheimer factor [19] and a is the nearest-neighbour distance. The Bose factor in Eq. (3), $n_i \equiv n(\varepsilon_{\lambda_i})$, can be expressed by

$$n_1 (n_2 + 1) = \frac{1}{4 \sinh^2(\beta \varepsilon_{\lambda}/2)}, \quad (7)$$

where $\beta = 1/k_B T$ is the inverse temperature of the lattice.

To numerically evaluate the expression (3) we make some assumptions and use the following procedures:

(a) We replace the summation $\sum_{\lambda} \dots$ by an integration $\int_0^{\nu_{max}} d\nu_{\lambda_i} G(\nu_{\lambda_i}) \dots$ over the total phonon density of states $G(\nu)$ up to ν_{max} , the maximum allowed frequency;

(b) We adopt the isotropic approximation for the wave vector $\omega = kv_D$, since in most cases we have $ka \ll 1$;

(c) In δ function, we neglect the nuclear resonance frequency for most phonon $\nu_0 \ll \nu_{\lambda_i}$;

(d) Finally, we consider in Eqs. (3) and (5) $\nu_{\lambda_1} \simeq \nu_{\lambda_2}$, $\xi_{k_1} \simeq \xi_{k_2} \equiv \xi_k$, $G(\nu_{\lambda_1}) \simeq G(\nu_{\lambda_2}) \equiv G(\nu)$.

After (a) – (d), one obtains an expression similar to formula (4) in the 1967 work of Bridges and Clark [20]:

$$W_{1R} = 2c \int_0^{\nu_{max}} F(\nu) d\nu, \quad (8)$$

where

$$F(\nu) = \frac{G^2(\nu) \nu^2}{\sinh^2(\beta h \nu / 2)}, \quad (9)$$

and c is a constant,

$$c = \frac{3}{10} \left(\frac{\pi e Q}{N M v_D^2} \right)^2 (d_1^2 + 4d_2^2) \frac{2I + 3}{(2I)^2 (2I - 1)}. \quad (10)$$

The presence of phononic band gap (PBG) [21, 22] in the phonon density of states of NaI, KI, NaBr, KBr and RbCl crystals makes it possible to subdivide Eq. (8) into two parts, one

expressing the contribution of acoustic phonons in quadrupolar SLR process and the other the contribution of optical phonons:

$$W_{1R} = W_{1R}^{\text{act}} + W_{1R}^{\text{opt}}, \quad (11)$$

with

$$W_{1R}^{\text{act}} = 2c \int_0^{\nu_{\text{max}}^{\text{act}}} \frac{G_{\text{act}}^2(\nu) \nu^2}{\sinh^2(\beta \hbar \nu / 2)} d\nu, \quad W_{1R}^{\text{opt}} = 2c \int_{\nu_{\text{min}}^{\text{opt}}}^{\nu_{\text{max}}^{\text{opt}}} \frac{G_{\text{opt}}^2(\nu) \nu^2}{\sinh^2(\beta \hbar \nu / 2)} d\nu, \quad (12)$$

where $G_{\text{act}}(\nu)$ and $G_{\text{opt}}(\nu)$ are the acoustic and the optical branches of PDOS, respectively; $\nu_{\text{max}}^{\text{act}}$ is the cut-off frequency of acoustic vibrations; $\nu_{\text{min}}^{\text{opt}}$ and $\nu_{\text{max}}^{\text{opt}}$ are the minimal and the maximal frequencies delimiting the optical vibrations.

These findings extend our knowledge of pure quadrupole relaxation and enable us to study the temperature dependence of each contribution and its individual quantitative importance in the relaxation process.

If we use the Debye phonon density of states, $G_{\text{Deb}}(\nu) = 9N\nu^2/(2\pi\nu_D^3)$, where ν_D is the Debye cut-off frequency, we get Eq.[9.6] from the VK and Walker [14] paper:

$$W_{1R} = 1.26 \pi \omega_D (d_1^2 + 4d_2^2) \frac{2I + 3}{I^2(2I - 1)} \left(\frac{eQ}{M\nu_D} \right) (T^*)^2 E^*(T^*), \quad (13)$$

where $T^* = k_B T / \hbar \omega_D$ and the function $E^*(T^*)$ has the different low- and high-temperature definitions:

$$\begin{aligned} T^* < 0.02 : \quad E^*(T^*) &= 1.4 \cdot 10^4 (T^*)^5 \times [1 - 340 (T^*)^2 + \dots] ; \\ T^* > 0.5 : \quad E^*(T^*) &= 1 - 0.056 (T^*)^{-2} . \end{aligned}$$

As in Ref. 14, once the transitions probabilities W_1 , W_{1R}^{act} and W_{1R}^{opt} become available, we can obtain the nuclear quadrupolar SLR time T_1 using the simple relationship,

$$T_1 = W_{1R}^{-1}. \quad (14)$$

By putting in Eq. (7) the lattice temperature values ranging between 20 and 300 K, similar calculations with realistic $G(\nu)$ can be performed. For NaI crystals we outline below the results obtained for 20, 40, 77, 100, 160, 200, 240, and 300 K. The temperature dependences of $W_{1R}^{\text{act}}(T)$, $W_{1R}^{\text{opt}}(T)$ and $T_1(T)$ for both ^{23}Na and ^{127}I nuclei are plotted. To compare these calculations with predictions from the Debye-model, expression (12) is used to plot in figure 6 below the theoretical $W_{1R}^{\text{Deb}}(T)$ and $T_1^{\text{Deb}}(T)$ curves over the same temperature range (20 –

300 K). Unfortunately, since experimental results of temperature dependence of quadrupolar SLR time $T_1^{Exp}(T)$ in alkali-halides and solids are scarce, we limited our comparisons to NaI. Experimental data for ^{23}Na and ^{127}I are taken from Ref. [7].

III. RESULTS AND DISCUSSIONS

A. Phonon Density of states

Figure 1 shows the phonon density of states $G(\nu)$ of NaI crystal calculated at room temperature with the force field computer code GULP [16], and by using the Catlow set parameters [17] for the pairwise potential of Eq. (1). The integration of PDOS in 1BZ was performed using a standard scheme for choosing the grid points developed by Monkhorst and Pack [18], which is incorporated in GULP code. In Fig. 1, a finite frequency field with a zero phonon density of states, the PBG explained by the large difference in the atomic mass of sodium Na and iodide I ions [23]. In our case the ionic mass ratio is about 5.5 (Tab. 3).

The separation between “acoustic” low-frequency region $G_{\text{act}}(\nu)$ and “optical” high-frequency region $G_{\text{opt}}(\nu)$ in Fig. 1 is estimated at 1.23 THz. Inelastic neutron scattering studies [24] suggest that the PBG is about 5 meV $\approx$ 1.203 THz in this crystal. By simple trapezoid integration, we verified that the optical and acoustic regions of the PDOS have equal areas as suggested for the true PDOS [22]. In the very low-frequency acoustic region ranging from 0 to 1.13 THz, the acoustic phonon density of states $G_{\text{act}}(\nu)$ practically coincides with the Debye function $G_{\text{Deb}}(\nu)$. The strong peak around 3.78 THz in the optical region $G_{\text{opt}}(\nu)$ is attributed to the transverse mode of lattice vibrations, which decreases rapidly while optical mode intensities are attenuated through the rest of the broad frequency interval.

Figure 2 displays a calculated PDOS function of NaCl crystal at room temperature obtained with the same lattice dynamics code. Comparing our PDOS in Fig. 2 or in Fig. 1 with early calculations [24–29], one finds that the Van Hove singularities [30] are located practically at the same positions as shown in Table 1.

FIG. 1. Phonon density of states of NaI crystal obtained at room temperature with the GULP code. Dashed curve represents a corresponding Debye function with cut-off frequency ν_D .

FIG. 2. The same as in Fig. 1, for NaCl.

Crystals	Singularities	Present work	Other	
NaCl	1	2.55	2.61 ^a	2.54 ^b
	2	3.42	3.52 ^a	3.53 ^b
	3	4.3	4.2 ^a	4.16 ^b
	4	5.14	4.92 ^a	5.18 ^b
	5	7	-	6.82 ^b
NaI	1'	1.12	1.15 ^c	1.23 ^d
	2'	1.55	1.49 ^c	1.53 ^d
	3'	2.36	2.4 ^c	2.38 ^d
	4'	3.78	3.75 ^c	3.61 ^d
	5'	5.67	5.2 ^c	5.3 ^d

TABLE 1. Comparison of the location of the PDOS singularities in NaCl and NaI crystals with other theoretical results: ^aRef. [27], ^bRef. [28], ^cRef. [24], ^dRef.[25].

B. Spin-Lattice Relaxation Time T_1

1. Case of crystals with PBG

Similarly to the NaI crystal, the KI, KBr, and NaBr crystals have a large mass ratios. Consequently, a marked separation between acoustic and optical branches with appreciable PBG is a feature of these crystals as well. Therefore, the transition probabilities W_{1R}^{act} and W_{1R}^{opt} in Eq. (11) for the total spin-lattice relaxation rate W_{1R} can be computed through numerical integration

$$W_{1R}^{\text{act}} = 2c \int_0^{\nu_{\text{max}}^{\text{act}}} F_{\text{act}}(\nu) d\nu, \quad (15)$$

$$W_{1R}^{\text{opt}} = 2c \int_{\nu_{\text{min}}^{\text{opt}}}^{\nu_{\text{max}}^{\text{opt}}} F_{\text{opt}}(\nu) d\nu, \quad (16)$$

where $F_{\text{act}}(\nu) = G_{\text{act}}^2(\nu)\nu^2/\sinh^2(\beta h\nu/2)$ and $F_{\text{opt}}(\nu) = G_{\text{opt}}^2(\nu)\nu^2/\sinh^2(\beta h\nu/2)$.

In Figure 3, the functions $F_{\text{act}}(\nu)$ and $F_{\text{opt}}(\nu)$ are plotted against vibrational frequency ν using $G_{\text{act}}(\nu)$ and $G_{\text{opt}}(\nu)$ obtained from GULP code. In the (a) panel of Fig. 3, the function $F_{\text{Deb}}(\nu)$ that would be obtained using a Debye phonon density of states $G_{\text{Deb}}(\nu)$ is shown

FIG. 3. The F_{act} (a) and the $F_{\text{opt}}(\nu)$ (b) functions of ν , calculated for the NaI crystal at room temperature. In the (a) panel, also the $F_{\text{Deb}}(\nu)$ function is also shown.

for comparison.

For all the crystals that we have already mentioned, viz: KI, KBr, and NaBr, the curves of the same type as in Fig. 3 were plotted. The areas under these curves were evaluated by the trapezoid method to be used in Eqs. (15), (16) and (14) for calculating the spin-lattice relaxation T_1 . Similar curves were also plotted at temperatures $T = 20, 40, 77, 100, 130, 160, 200$, and 240 K for NaI to calculate the temperature dependence of quadrupolar SLR time for ^{23}Na and ^{127}I nuclei. The functions $F_{\text{act}}(\nu)$ and $F_{\text{opt}}(\nu)$ at $T = 20$ K are plotted in Fig. 4. To compare Fig.3 with Fig.4, one can calculate the relative decrease of areas under each curve A : $A_{\text{act}}(20 \text{ K})/A_{\text{act}}(\text{RT}) \approx 1.5 \times 10^{-3}$; $A_{\text{opt}}(20 \text{ K})/A_{\text{opt}}(\text{RT}) \approx 4.6 \times 10^{-5}$. These ratios indicate that at low temperature, the Bose factor defined by Eq. (7) reduces the phonon optical contribution in the relaxation process more significantly, by almost two orders of magnitude than the acoustic contribution.

In Table 2, we present the following results for quadrupolar SLR time at room temperature: our T_1 calculated with the real phonon spectrum, the T_1^{Deb} obtained by VK – Walker[31] within the Debye-model, and the experimental values T_1^{Exp} of Refs. 5 and 31. The third and the fourth columns contain the calculated values of the Raman transition probabilities W_{1R}^{act} and W_{1R}^{opt} by Eqs (15) and (16) respectively. With the aim of comparing the Debye-model estimate against the realistic phonon spectrum-based prediction, the ex-

FIG. 4. Calculated $F_{act}(\nu)$ function (a) and $F_{opt}(\nu)$ function (b) in NaI at $T=20$ K .

Crystal	Nucleus	W_{1R}^{act} (s ⁻¹)	W_{1R}^{opt} (s ⁻¹)	T_1 (s)	T_1^{Deb} (s)	T_1^{Exp} (s)	T_1^{Deb}/T_1^{Exp}	T_1/T_1^{Exp}
KBr	⁷⁹ Br	0.0646	0.0774	7.04	18.72	0.072	260	98
NaBr	⁷⁹ Br	0.18	0.19	2.7	5.2	0.052	100	52
	²³ Na	0.0013	0.0013	370	2400	6	400	61
NaI	²³ Na	0.002	0.006	123	3850	5	770	24
	¹²⁷ I	0.7	2.03	0.36	6.84	0.012	570	30
KI	¹²⁷ I	0.27	0.45	0.72	15.2	0.019	800	38

TABLE 2. Acoustic W_{1R}^{act} and optical W_{1R}^{opt} contributions to Raman relaxation process in alkali halides and hence derived relaxation time calculated with realistic PDOS (T_1), on the basis of the Debye model (T_1^{Deb}), and cited from experiments[5, 31] (T_1^{Exp}). See text for details.

cess of each of these results over the nominal experimental value is shown in the last two columns of the table. The crystal and nuclear constants used in the calculations are shown in Table 3.

From Table 2, we see that the calculated relaxation times T_1 considerably smaller than the values obtained by VK – Walker T_1^{Deb} , and “only” by an order of magnitude (see last column of Table 2) exceed the experimental results. We note that earlier theoretical studies [2–4] done within the framework of the point charge model yielded the relaxation times values

Crystal	Nucleus	$a_0(\text{\AA})$	$v_D \times 10^5 \text{ cm s}^{-1}$	$\nu_D \text{ THz}$	$M \times 10^{-24} \text{ g}$	$Q \times 10^{-24} \text{ cm}^2$	γ
KBr	^{79}Br	6.59	2.48	2.33	132.64	0.3	86.512
NaBr	^{79}Br	5.97	2.53	2.62	132.64	0.3	86.512
	^{23}Na	5.97	2.53	2.62	38.16	0.1	6.452
NaI	^{23}Na	6.47	2.07	1.98	38.16	0.1	6.452
	^{127}I	6.47	2.07	1.98	210.66	-0.79	163.42
KI	^{127}I	7.06	1.94	1.71	210.66	-0.79	163.42
NaCl	^{23}Na	5.64	3.36	3.69	38.16	0.1	6.452
	^{35}Cl	5.64	3.36	3.69	58.87	0.081	42.999
KCl	^{35}Cl	6.29	3.03	2.99	58.87	0.081	42.999
RbBr	^{79}Br	6.86	2.05	1.85	132.64	0.3	86.512

TABLE 3. Crystal and nuclear constants used in the relaxation time calculation. The values of the Sternheimer anti-shielding factor γ in the last column are from Ref. 33.

larger than the experimental ones by a factor of $10^2 - 10^3$. We consider our results very reasonable for this model, and the slight divergence from experiment can be linked to other effects such as covalency [3], overlap [4], ionic polarizability [5] and lattice anharmonicity [31].

The use of realistic phonon spectrum makes it possible to quantitatively distinguish the contributions of acoustic and optical phonons in the relaxation process. From the third and fourth columns in Table 2, it appears that for ^{79}Br and ^{23}Na nuclei in KBr and NaBr crystals both contributions have the same intensity. However, in NaI crystals the optical phonon contribution is threefold greater than the acoustical one. Calculations confirm the sensitivity of T_1 to the PDOS, and are useful in the validation of different lattice models and approximations.

Fig. 5 shows the temperature dependence in the range 2- – 300 K of acoustic W_{1R}^{act} and optical W_{1R}^{opt} contributions in Quadrupolar SLR (a) for sodium and (b) for iodide nuclei in NaI crystal. Within the lower temperature range (20 – 77 K), where only a few optical phonons are thermally excited, the transition probabilities of both contributions practically have equal values. Above 100 K, the optical contribution W_{1R}^{opt} begins to increase faster than the acoustic contribution, and near 250 K an inflection is observed in both curves, probably

FIG. 5. Temperature dependence of acoustic W_{1R}^{act} (lower set, circles) and optical W_{1R}^{opt} (upper set, squares) contributions in Quadrupolar SLR process for sodium (a) and iodine (b) nuclei in the NaI crystal.

FIG. 6. Temperature dependence of T_1 for the ^{23}Na nuclei in the NaI crystal, calculated according to the Debye-model (upper curve, triangles), calculated using the realistic PDOS (middle curve, circles) and after the experimental data of Ref. 7.

due to the Bose factor (Eq. 7). These observations equally apply to both the sodium and the iodine nuclei.

In the range 50 – 300 K, the temperature dependences of quadrupolar SLR time T_1 of

FIG. 7. Same as in Fig. 6, for the ^{127}I nuclei in NaI.

^{23}Na and ^{127}I nuclei in NaI crystal are shown in Figs. 6 and 7. For the sake of comparison, we plotted the calculated values T_1^{Deb} from Debye function and the measured T_1^{Exp} (Ref. 7) depending on temperature. Our calculation matched with the experimental data for both nuclei in the high temperature region beginning at 200 K. This is a manifestation of a systematic increase of optical contributions W_{1R}^{opt} with temperature, as is seen in Fig. 5. Needless to say, the results for ^{127}I are somewhat better than for ^{23}Na . As an example, in the temperature range 240 – 300 K, the disagreement with the experimental values for iodine nuclei is approximately 5% while for sodium it is near 11%. Following Ref. 5, a nuclei surrounded by ions with large polarizability, such as iodine of polarizability ~ 6.35 [32], are more strongly coupled to the optical phonons than the nuclei whose neighbours' polarizability is small, e.g., ~ 0.147 for ^{23}Na . Therefore, the results for ^{23}Na must be corrected with the leading induced dipole mechanism proposed by Ref. 5.

A satisfactory agreement between experimental results and our T_1 calculation in a wide temperature range confirms that the PDOS obtained by GULP is realistic. It is apparent from Figs 6 and 7 that the Debye model is in strong disagreement with experimental data for both nuclei at any temperature. For temperatures below 150 K, our curves diverge from experimental values, and we obtain longer relaxation times. We assume that, at lower temperature, the role of different unavoidable lattice defects becomes important in spin-lattice relaxation processes which leads to shorter experimental relaxation times.

FIG. 8. The calculated room temperature phonon function $F(\nu)$ of sodium chloride and the corresponding $F^{Deb}(\nu)$.

2. Case of crystals without PBG

Let us now consider typical alkali halides such as NaCl, KCl and RbBr for which a phononic band gap is not observed. The calculation method of relaxation time T_1 is identical to the earlier method (Eqs (15) and (16)), only that it is not anymore possible to separate the contributions from optical and acoustical phonon modes. Using the general expression (Eq. 8), one can determine the transition probability of the Raman process W_{1R} by integration of $F(\nu)$ (Eq. 9) over the total PDOS. The calculations were done for ^{23}Na in sodium chloride, ^{79}Br in rubidium bromide and for ^{35}Cl in NaCl and KCl crystals.

The calculated room temperature phonon function $F(\nu)$ of sodium chloride is shown in Fig.8. Analogous curves were also plotted for KCl and RbBr crystals. Numerical values of transition probabilities W_{1R} , relaxation time T_1 and their corresponding T_1^{Deb} and T_1^{Exp} are shown in Tab. 4. From the last two columns of (Tab. 2 and Tab. 4), we can conclude that our calculations for this case are better, and the agreement with experiment is good. As the Debye function is insensitive to the PBG, there seems to be no improvement in results for T_1^{Deb} . Noteworthy, an excellent agreement is obtained for ^{35}Cl in both NaCl and KCl, probably due to the important Sternheimer anti-shielding factor γ (Tab. 3).

Crystal	Nucleus	W_{1R} (s ⁻¹)	T_1 (s)	T_1^{Deb} (s)	T_1^{Exp} (s)	T_1^{Deb}/T_1^{Exp}	T_1/T_1^{Exp}
NaCl	²³ Na	0.00117	854	3960	12	330	71
	³⁵ Cl	0.0147	67.93	1920	5.2	370	13
KCl	³⁵ Cl	0.0108	92.59	3910	8.5	460	11
RbBr	⁷⁹ Br	0.2	5	29	0.085	350	59

TABLE 4. Calculated transition probabilities of Raman relaxation process W_{1R} based on real PDOS, $T_1 = W_{1R}^{-1}$ derived relaxation times, T_1^{Deb} relaxation times calculated by Debye function (Ref. 31) and T_1^{Exp} – experimental values from Refs. 5 and 31.

IV. CONCLUSION

The inclusion of real phonon density of states in the original VK treatment leads to improvements in the ionic-point model of nuclear quadrupolar relaxation in solid alkali halides. Our calculations T_1 for nuclei in crystals with phononic band gap (NaI, KI, KBr and NaBr) elucidate the role of each phononic branch in the relaxation process. Over the temperature range 20 – 300 K, T_1 calculated as function of temperature for ²³Na and ¹²⁷I is in good agreement with experiment, particularly at high temperature ($T > 77$ K). In alkali halides, the Debye phonon function does not yield satisfactory results for relaxation time at room temperature as it ignores the optical phonons. Consequently, the Debye-model isotropic dispersion $\omega(\vec{k})$ must be replaced by a realistic dispersion relation, obtained from lattice dynamic calculation. Such a task, even if tedious, seems to improve our comprehension of experimental results and the general mechanisms of quadrupole relaxation in solids. Furthermore, careful T_1 measurements over a wide temperature range with highly pure samples would be required to obtain quantitative information about both the quadrupole relaxation and the phonon spectrum. Finally, a calculation using phonon Green's function method might be able to confirm the predicted values of the relaxation time.

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