

Calculation of NQR ν 's and T_1^{-1} 's being proportional to T^4 and T^5 , respectively *

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The second-order Raman phonon process for a multilevel spin system is shown to give a quadrupolar spin-lattice relaxation rate T_1^{-1} varying as T^5 at very low temperatures. This relaxation rate for quadrupole spins is similar to the one discussed for a paramagnetic spin system having a multilevel ground state. The temperature dependence of T_1 is discussed on the basis of some simplifying assumptions about the nature of the lattice vibrations in the Debye approximation. This type of relaxation process has been observed below 20 K in tetramethylammonium hydrogen bis-trichloroacetate for the ^{35}Cl T_1^{-1} . Below 20 K the NQR frequency in the same crystal reveals a T^4 temperature dependence due to the induced modulations of the vibrational and librational coordinates by the low-frequency acoustic phonons.

Key words: Quadrupole relaxation, low temperature, NQR.

Introduction

Nuclear quadrupole spin-lattice relaxation in a crystalline solid comes about as the result of an exchange of energy between the nuclear spin system and the lattice vibrations. A theory for quadrupole nuclear spin-lattice relaxation in crystalline ionic solids was first discussed by Van Kranendonk [1] and Van Kranendonk and Walker [2]. The crystalline electric field gradient (EFG) was calculated using a point-charge model and its variation due to the influence of thermal modulation of the crystalline field, in the Debye approximation. The relaxation theory based on analysis of thermal vibrations in an ionic lattice shows that the quadrupole relaxation is determined mainly by the Raman process (the emission of one phonon and absorption of another). The reason for the relative importance of the Raman process is that all the phonons of the spectrum may take part in it. The characteristic feature of the Raman process is its temperature variation of the relaxation rate, which can

yield information about the possible relaxation processes. The first-order phonon Raman process (the inelastic scattering of a phonon by the spin system) leads to a T^2 temperature dependence at high temperatures ($T > T_D/2$) and a T^7 temperature dependence at low temperatures [1].

However, there are not many experimental determinations of the quadrupole relaxation at low temperatures ($T < 50$ K). The literature lacks systematic studies of the low temperature effect on the quadrupole relaxation as well as the NQR frequency. Recently, it was shown that the ^{35}Cl quadrupole spin-lattice relaxation rate T_1^{-1} varies as T^5 at low temperatures [3, 4]. This behaviour cannot be explained by the existing theories based on the first-order Raman process. The primary purpose of this work is to establish the mechanism driving the quadrupole spin-lattice relaxation arising from the interaction of the nuclear electric quadrupole moment with the crystalline electric field and leading to the T^5 -dependence. The temperature dependence of the second-order Raman process is determined on the basis of some simplifying assumptions about the nature of the lattice vibrations in the Debye approximation. It is shown that this new mechanism (similar to the one discussed by Orbach and Blume [5], and Walker [6] for multilevel paramagnetic ions) gives a quadrupolar spin-lattice relaxation rate (T_1^{-1}) varying as T^5 at low temperatures.

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Furthermore, at low temperatures the NQR frequencies reveal a dominant T^4 temperature dependence due to the induced modulations of the vibrational and librational coordinates by the low-frequency acoustic phonons. We have observed this effect in tetramethylammonium hydrogen bis-trichloroacetate $[\text{N}(\text{CH}_3)_4\text{H}(\text{Cl}_3\text{CCOO})_2]$ for temperatures below 20 K. The obtained NQR-frequency data analyzed on the basis of the theory of Schempp and Silva [7].

Nuclear Quadrupole Spin-lattice Relaxation

The relaxation process considered in this work is the second-order Raman process illustrated in Figure 1. The quadrupolar nucleus which is initially in the state $|a\rangle$ absorbs the phonon λ_1 while making a transition to the intermediate state $|m\rangle$ and then emits a phonon λ_2 while making a transition to its final state $|b\rangle$. Orbach and Blume [5] have pointed out that for the case of a spin system having a multilevel ground state, the Raman process operates through an intermediate state $|m\rangle$ within the multilevel state.

The combined Hamiltonian of the spin system and the lattice is a sum of three terms, one describing the spin system, one the lattice, and one the interaction between the spin system and the lattice; thus

$$H = H_S + H_L + H_{SL}(t), \quad (1)$$

where H_S is a time independent spin-Hamiltonian, H_L a time independent lattice-Hamiltonian and $H_{SL}(t)$ a time dependent spin-lattice interaction. The Hamiltonian which describes a nuclear quadrupole interaction is

$$H_Q(t) = \frac{eQ}{4I(2I-1)} \sum_{l=-2}^2 V_l(t) I_{-l}, \quad (2)$$

where $V_l(t)$ is a time-dependent lattice operator and I_l is a spin operator. More specifically

$$\begin{aligned} V_0 &= V_{zz}, & I_0 &= 3I_z^2 - I^2, \\ V_{\pm 1} &= V_{zx} \pm iV_{zy}, & I_{\pm 1} &= I_{\pm} I_z + I_z I_{\pm}, \\ V_{\pm 2} &= \frac{1}{2}(V_{xx} - V_{yy}) \pm iV_{xy}, & I_{\pm 2} &= (I_{\pm})^2, \end{aligned} \quad (3)$$

where $V_{\alpha\beta}$ is an element of the tensor and I_z, I_{\pm} are the familiar spin operators. For this case H_S is the secular part of $H_Q(t)$,

$$H_S = \overline{H_Q(t)} = \sum_m E_m |m \times m|. \quad (4)$$

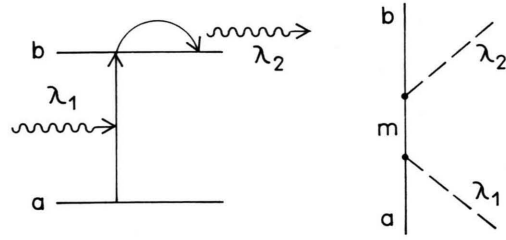


Fig. 1. The second-order Raman relaxation process and its Feynman diagram.

The quadrupolar nucleus has energy levels E_m and eigenstates $|m\rangle$. E_m and $|m\rangle$ are computed taking into account only the static crystalline EFG at the nucleus. The basic problem of the relaxation theory is to calculate the transition rates between these levels due to the lattice vibrations.

The spin-lattice Hamiltonian $H_{SL}(t)$ is the non-secular part of $H_Q(t)$:

$$H_{SL}(t) = H_Q(t) - \overline{H_Q(t)} = \sum_{mm'ix} F_{mm'ix} |m \times m'| u_{ix}, \quad (5)$$

where u_{ix} is the nuclear displacement. The subscript i labels the Bravais lattice sites and $\alpha = x, y, \text{ or } z$. The components of the spin-lattice interaction Hamiltonian are expanded in powers of the nuclear displacements. For our purpose it will be sufficient to retain only the terms linear in the u_{ix} .

Using the standard normal coordinate transformation (cf. e.g. [8]) the lattice Hamiltonian and the spin-lattice interaction can be written in the form

$$H_L = \sum_{\lambda} (a_{\lambda}^{\dagger} a_{\lambda} + \frac{1}{2}) E_{\lambda}, \quad (6)$$

and

$$H_{SL} = \sum_{mm'\lambda} F_{mm'\lambda}(\lambda) |m \times m'| A_{\lambda}, \quad (7)$$

where E_{λ} is the energy of the phonon labeled by the index λ , and $A_{\lambda} = a_{\lambda}^{\dagger} + a_{\lambda}$, where a_{λ}^{\dagger} and a_{λ} are the phonon creation and annihilation operators.

The transition probability per unit of time of the transitions between the eigenstates $|a\rangle$ and $|b\rangle$ of the zeroth order Hamiltonian $H_S + H_L$ ($|a\rangle$ and $|b\rangle$ are eigenstates of H_S , whereas $|p\rangle$ and $|p'\rangle$ are eigenstates of H_L) is given by

$$\begin{aligned} w_{ap \rightarrow bp'} &= (2\pi/\hbar) \left| \langle b p' | H_{SL} \frac{1}{E_a + E_p - H_S - H_L} H_{SL} | a p \rangle \right|^2 \\ &\cdot \delta(E_a + E_p - E_b - E_{p'}). \end{aligned} \quad (8)$$

In (8) only the second-order matrix elements in H_{SL} are shown since it are only these terms which give rise to the second-order Raman process we wish to study. The terms linear in H_{SL} , which are responsible for the direct process, have been omitted. T_1^{-1} equals $2 w_{a \rightarrow b}$, where $w_{a \rightarrow b}$ is the transition probability (8) averaged over all initial states and summed over all final states of the lattice, i.e.

$$w_{a \rightarrow b} = \sum_{p p'} P_p w_{a p \rightarrow b p'}, \quad (9)$$

where P_p is the probability that the lattice is in the state $|p\rangle$ at a given temperature, and P_p depends on the energies of the lattice eigenstates.

Combining (8) and (9), it is found that the transition probability $w_{a \rightarrow b}$ for the second-order Raman process illustrated in Fig. 1 is given by

$$w_{a \rightarrow b} = \frac{2\pi}{\hbar} \sum_{\lambda_1 \lambda_2} n_{\lambda_1} (n_{\lambda_2} + 1) \cdot \left| \sum_m \left\{ \frac{F_{bm}(-\lambda_2) F_{ma}(\lambda_1)}{E_a - E_m - \hbar \omega_{\lambda_1}} + \frac{F_{bm}(\lambda_1) F_{ma}(-\lambda_2)}{E_a - E_m - \hbar \omega_{\lambda_2}} \right\} \right|^2 \cdot \delta(E_a - E_b + \hbar \omega_{\lambda_2} - \hbar \omega_{\lambda_1}), \quad (10)$$

where n_λ represents the thermal averaged population of the lattice mode λ (the Bose-Einstein occupation number). The first term in the sum inside the curly bracket in (10) comes from processes in which the phonon λ_1 is absorbed before the phonon λ_2 is emitted, whereas the second comes from processes in which the phonon λ_2 is emitted before the phonon λ_1 is absorbed. The sum can be restricted to $m=a, b$ because there is no higher energy levels of the quadrupolar nucleus in the energy range investigated. Since m is one of the ground levels, the following condition is fulfilled: $|E_a - E_m| \ll kT$. This means that phonons with energies $\hbar \omega_\lambda \gg |E_a - E_m|$ will give the most important contribution to the sum over λ_1 and λ_2 . In general, when the excited-state energy is very small compared to the energy of the most important phonons involved in the relaxation process, the denominator in (10) may be approximated by $\hbar \omega_\lambda$. Thus (10) can be written in the form

$$w_{a \rightarrow b} \approx \frac{2\pi}{\hbar} \sum_{\lambda_1 \lambda_2} \frac{n_{\lambda_1} (n_{\lambda_2} + 1)}{(\hbar \omega_{\lambda_1})^2} \cdot \left| \sum_m \{ F_{bm}(-\lambda_2) F_{ma}(\lambda_1) - F_{bm}(\lambda_1) F_{ma}(-\lambda_2) \} \right|^2 \cdot \delta(\hbar \omega_{\lambda_1} - \hbar \omega_{\lambda_2}). \quad (11)$$

The explicit calculation of the sum over $m=a, b$ in (11) is rather complicated. The values and symmetry properties of the spin-lattice coupling coefficients F depend on details of the particular spin system and the crystal structure. However, we are interested mainly in finding the temperature dependence of T_1^{-1} in the region of practical importance, i.e. at temperatures well below the Debye temperature.

At low temperatures, only low-energy, long-wavelength phonons are important. The Debye approximation will be made and the same velocity of sound will be assumed for all branches of the phonon spectrum. Details of the calculations will be omitted because a similar procedure is described in [9] where the phonon energy densities and their temperature dependences are calculated. Using the Debye approximation and replacing the double summation in (11) by the double integration, one obtains the transition probability for the second-order Raman process:

$$w_{a \rightarrow b} \sim \int_0^{\omega_D} \frac{\omega^4 \exp(\hbar \omega / kT)}{[\exp(\hbar \omega / kT) - 1]^2} d\omega \sim T^5 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (12)$$

where $x = \hbar \omega / kT$. The integral over the lattice frequencies reaches from 0 to the Debye frequency but at low temperatures, where such frequencies are not excited, there is no significant error in replacing the upper limit by infinity. Thus this integral can be approximated by

$$\int_0^\infty x^4 e^{-x} dx = 4! \quad (13)$$

Therefore, T_1^{-1} is characterized by the temperature dependence

$$T_1^{-1} \sim T^5. \quad (14)$$

The integral in (12) can also be evaluated in the high temperature limit where kT is large compared with the maximum phonon energy $\hbar \omega_D$. Then, since $x \ll 1$,

$$T^5 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \approx T^5 \int_0^{x_D} x^2 dx \quad (15)$$

and we have

$$T_1^{-1} \sim T^2. \quad (16)$$

Therefore, the second-order Raman process leads to the T^2 dependence of T_1^{-1} on temperature in the high-temperature approximation. Van Kranendonk

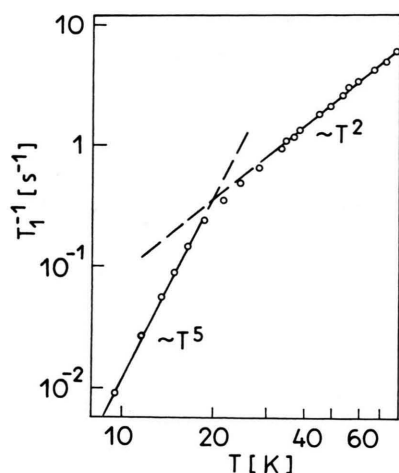


Fig. 2. Temperature variations of the ^{35}Cl quadrupole spin-lattice relaxation rate in tetramethylammonium hydrogen bis-trichloroacetate, $\text{N}(\text{CH}_3)_4\text{H}(\text{Cl}_3\text{CCOO})_2$. The slopes represent the Raman T^5 and T^2 dependences in the low-temperature region, respectively.

[1] and van Kranendonk and Walker [2] have shown that both the anharmonic and first-order Raman relaxation processes also exhibit the same temperature dependence in the high-temperature approximation. Thus a study of the temperature dependence of T_1 makes it impossible to distinguish between various relaxation mechanisms in this temperature region.

The temperature dependence of the ^{35}Cl quadrupole spin-lattice relaxation rate in $\text{N}(\text{CH}_3)_4\text{H}(\text{Cl}_3\text{CCOO})_2$ is shown in Fig. 2. This is one of the few examples in which the quadrupole relaxation rate shows different temperature dependences: T^5 and T^2 in distinct temperature ranges. For temperatures below 20 K, the ^{35}Cl NQR T_1^{-1} is proportional to T^5 as predicted by the second-order Raman phonon process. For higher temperatures (between ca. 25 and 130 K) the T_1^{-1} data obey instead the relation $T_1^{-1} \sim T^2$. Recently, also a relation $T_1^{-1} \sim T^5$ has been observed in $(\text{NH}_4)_2\text{SnCl}_6$ for temperatures below 20 K by Dimitropoulos et al. [4].

Nuclear Quadrupole Resonance Frequencies at low Temperatures

Schempp and Silva [7] have shown that the temperature dependence of NQR frequencies in solids includes a term proportional to T^4 which arises from the lattice acoustic modes.

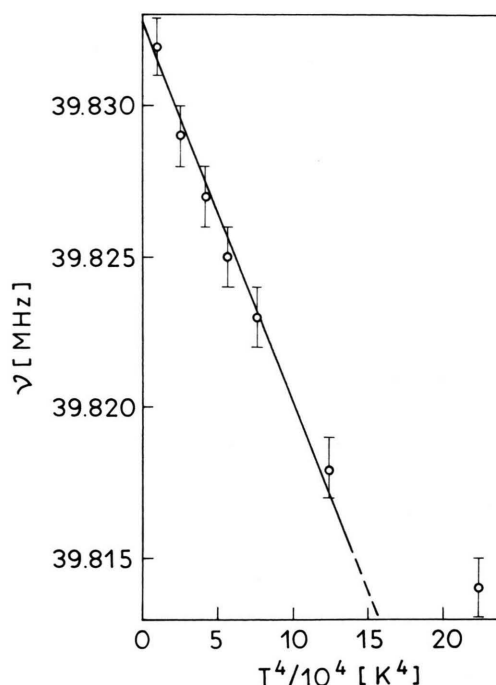


Fig. 3. ^{35}Cl frequency variation in tetramethylammonium hydrogen bis-trichloroacetate $\text{N}(\text{CH}_3)_4\text{H}(\text{Cl}_3\text{CCOO})_2$, plotted against T^4 in the low-temperature region. The best fit line to T^4 is given by (19).

In [7] it was shown that the temperature dependence of the NQR frequency is of the form

$$\nu - \nu_0 = - \left\{ AT^4 [J(x_D)/J(\infty)] + N^{-1} \sum_{l,\lambda} B_l(\lambda) [\exp(\hbar \omega_{\lambda l}/kT) - 1]^{-1} \right\}, \quad (17)$$

where

$$J(x_D) = \int_0^{x_D} x^3 (e^x - 1)^{-1} dx, \quad x_D = T_D/T, \quad (18)$$

$$J(\infty) = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} \approx 6.5.$$

T_D is the Debye temperature, ν_0 is the frequency at $T=0$, and the terms in B_l correspond to the librational-averaging model due to Bayer [10].

The Debye term of the form $AT^4 J(x_D)/J(\infty)$ comes from a modulation of the internal or librational coordinates of the group containing the quadrupole nucleus by the acoustic branch coordinates oscillating at the low acoustic branch frequencies. This modulation is proportional to the total energy $U(T)$ of the solid which goes as T^4 . The T^4 dependence can only

be expected to predominate at low temperatures where the Bayer term becomes exponentially small and negligible [7].

^{35}Cl NQR frequency ν in $\text{N}(\text{CH}_3)_4\text{H}(\text{Cl}_3\text{CCOO})_2$ plotted against T^4 is shown in Figure 3. The obvious curvature at high temperature becomes linear in T^4 below about 20 K. The best fit in T^4 is given by

$$\nu(T) = 39\,832.8 - 1.255 \cdot 10^{-4} T^4 [\text{kHz}]. \quad (19)$$

We conclude that the T^4 dependence is well demonstrated in the region $T < 20$ K. The value of the Debye term in (19) is of the same order as that found by Schempp and Silva [11] for several organic and inorganic crystals. This fact suggests that a low temperatures, the induced modulations of the vibrational and librational coordinates by low-frequency acoustic phonons is the dominant mechanism responsible for the temperature dependence of the NQR frequencies.

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