$T^H$-DEPENDENCE OF THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES IN SOLIDS (I)

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ABSTRACT

A discussion is presented on the mechanism that gives rise to the dominant $T^4$ dependence of the NQR frequencies at low temperatures observed in a number of solids. A simplified diatomic linear chain model is shown to display the essential ingredients. The uniform translational character of the acoustic phonons is shown to produce a $T^4$ dependent Doppler shift which is too small to account for the experimental results. The non-uniform, q-dependent character of the acoustic branch is shown to induce modulations of the librational and vibrational coordinates at the low frequencies.

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of the acoustic phonons, the only excitons traveling in the solid at low temperatures. The Bayer term and the Debye term are shown to be produced by the modulation of the same coordinates, except that they occur at different frequencies. Also shown is that the coefficient for the $T^4$ term may contain contributions involving crossed averages which are non-zero since they correspond to coordinates oscillating coherently at the same frequency.
Sixteen years ago Kushida, Benedek and Bloembergen\(^{(1)}\) predicted a term of the form

\[
A'T^4 \int_0^{T_D/T} \left( \frac{1}{2} + \frac{1}{\varepsilon^2 - 1} \right) x^3 dx
\]  

\[ (1) \]

in addition to the usual \( \text{Ba} \)\text{uer}\(^{(2)}\) term, for the temperature dependence of the NQR frequencies in solids. In that paper the above term was then succinctly described as due to the "Debye waves".

With the detection\(^{(3)}\) of a dominant \( T^4 \) dependence at low temperatures \( T \leq 35^\circ K \) in a number of solids, it becomes now necessary to obtain a clearer understanding about the mechanism that gives rise to this term as well as on its importance for the correct interpretation of NQR data in the high temperature region.

A theory\(^{(4)}\) based on the external modes approximation\(^{(5)}\) has been developed for the temperature dependence of the NQR frequencies, where particular attention is given to the \( T^4 \) Debye term.

It is the purpose of this letter to discuss a simplified model in order to display the essential ingredients of the problem.

First of all, let us point out that the Debye waves, i.e., the translational acoustic phonons are unable, by themselves, to affect directly the electric field gradient (EFG) at the quadrupole nucleus. This fact is a result of the invariance of the EFG under uniform translations which represent the dominant feature of the acoustic vibrations in the long wave length limit\(^{(6)}\). The only direct
effect produced by the translational acoustic lattice vibrations is a kinematic, second-order, relativistic Doppler effect whereby the r.f. frequency undergoes a shift $\Delta v$ when absorbed by the moving quadrupole nucleus. The Doppler shift is given by

$$\frac{\Delta v}{v} = -\frac{v}{c} + \frac{1}{2} \left( \frac{v}{c} \right)^2,$$

where $v$ is the velocity of the quadrupole nucleus and $c$ is the velocity of light. Taking into account that the thermal average $\langle v \rangle = 0$, and that

$$\langle v^2 \rangle = \frac{1}{N} \sum \frac{1}{q} \left( \frac{\hbar \omega}{q} \right)^2 \langle u^2 \rangle,$$

where

$$\langle u^2 \rangle = \frac{1}{m} \sum \frac{1}{q} \frac{\hbar \omega}{q} \langle u^2 \rangle,$$

and

$$\hbar \omega = N \omega_q,$$

for a q-component of $u$, one obtains

$$\langle v^2 \rangle = \frac{1}{N} \sum \frac{1}{q} \left( \frac{\hbar \omega}{q} \right)^2 \langle u^2 \rangle = \frac{1}{m} \frac{1}{N} \sum \frac{1}{q} \frac{\hbar \omega}{q} \langle u^2 \rangle \propto U(T) \quad (2)$$

where

$$\langle u^2 \rangle = \frac{1}{N} \sum \frac{1}{q} \left( \frac{\hbar \omega}{q} \right)^2 \langle u^2 \rangle.$$

As a result

$$\frac{\Delta v}{v} \propto \langle v^2 \rangle$$

in eq. (2) is proportional to the total lattice vibrational energy $U(T)$, producing a $T^4$ dependence, corresponding to the well-known Debye $T^3$ law for the low temperature specific heat of solids. Actually, the Doppler term is too small to account for the observed frequency shifts. One can show that, for $T < T_D$, 

$$\left( \frac{\Delta v}{v} \right)_{\text{Doppler}} = \frac{1}{2} \frac{m \langle v^2 \rangle}{mc^2} < \frac{KT_D}{mc^2} \ll 10^{-12},$$

for a Debye temperature $T_D = 100^0K$ and $m$ equal to 20 nucleon masses. Even for $v = 100$ Mcps, one obtains 

$$\left( \frac{\Delta v}{v} \right)_{\text{Doppler}} < 10^{-7} \text{ kcps},$$

while the observed frequency shifts are of the order of 30 kcps for $T < 30^0$. 
The Doppler effect being discarded, it turns out that the dominant $T^4$ dependence at low temperatures is due to the association of two factors: (a) the absolutely overwhelming presence of translational acoustic phonons of long wavelength at low temperatures $T \ll T_D$; (b) the acoustic phonons present in the solid induce forced librations and vibrations at the very low frequencies $\omega_{qa}$ of the acoustic branches.

The statement (a) is a well-known result. The ratio of the number of phonons present in the solid, belonging to the acoustic and non-acoustic branches is given by $n_q/n_L \sim (KT/\hbar \omega_q)\exp(\hbar \omega_q/KT)\gg 1$ where $\omega_L$ is the frequency of the lowest, nearly flat, non-dispersive, librational, vibrational or translational optical branch. One can show that the amplitude of the indirect effect (b) is proportional to the small difference of displacements between one site and the next. In other words, the amplitude of induced libration or vibration is proportional to the small non-uniform character present in the translational acoustic branch.

See Fig.(1) and Fig.(2)

Fig. 1

Now, for an acoustic wave of momentum $q$, one can show that,
in the long wave-length limit,

\[ u_{2s+1} - u_{2s} \approx \frac{a}{2} \left( u_{2s} \right)^2 \left( \frac{\hbar \omega_{qa}}{\hbar c_s} \right) u_{2s} \]  \hspace{1cm} \text{(3)}

where \( a \) is a lattice distance, \( \overline{a} \) involves a ratio of elastic coupling constants, \( u_{2s}(t) = \text{const.}\cos(qx_{2s} - \omega_{qa} t) \) represents the oscillations of frequency \( \omega_{qa} \), and wave number \( q \), \( c_s \) being the velocity of sound in the solid. If the branch \( \omega_z \) is vibrational in character, one can write \( u_{\nu} = u_{2s+1} - u_{2s} \) (see fig.1a), or, from eq.(3),

\[ \langle u_{\nu}^2 \rangle \approx \left( \frac{\overline{a}}{\hbar c_s} \right)^2 \left( \frac{\hbar \omega_{qa}}{\hbar c_s} \right) \langle u_{2s}^2 \rangle \]  \hspace{1cm} \text{(4)}

i.e., a result similar to eq.(2), resulting in the same form of temperature dependence as the total energy of the lattice.

For a librational branch noting that \( \theta \approx \frac{1}{5}(u_{2s+1} - u_{2s}) \) (see fig.1b), one would again obtain an expression similar to eq.(2). In other words, all coordinates whose modulation is able to change the EFG, undergo forced oscillations at the frequencies of the acoustic phonons with the result that all averages \( \langle \theta^2 \rangle \), \( \langle \theta \nu \rangle \), \( \langle u_{\nu}^2 \rangle \), etc., present a temperature dependence similar to the total energy \( U(T) \) of the lattice due to phonons, i.e., with a dominant \( T^4 \) behavior at sufficiently low temperatures, as confirmed by experiment.
In order to clarify the essential elements for this $T^4$ dependence, let us consider a simple model, that of a diatomic linear chain (see fig. 2). Taking into account only nearest neighbor interactions, assume an intramolecular coupling constant $K$ and an intermolecular coupling $k$.

Assume also that the EFG at the moving quadrupole nucleus, say $A_1$, depends only on the modulation of the intramolecular distance $u_{2s+1} - u_{2s}$. This is an unnecessary assumption; in the more general case, the change in EFG produced by the lattice vibrations would depend also on $u_{2s} - u_{2s-1}$ (see fig. 2), which may be considered as the change of intermolecular distance; consequently the NQR frequency shift is of the form $\Delta v = a_{11} u_{2s+1} - u_{2s}^2 + a_{12} u_{2s+1} - u_{2s} (u_{2s} - u_{2s-1}) + a_{22} (u_{2s} - u_{2s-1})^2 + \ldots$ all these terms presenting the same $T^4$ dependence at low temperatures. For this reason let us concentrate our attention on the intramolecular distance $u_{2s+1} - u_{2s}$.

The equations of motion are given by (8)
\[ m_2 u_{2s+1} = K(u_{2s} - u_{2s+1}) + k(u_{2s+2} - u_{2s+1}) , \]

\[ m_1 u_{2s} = k(u_{2s-1} - u_{2s}) + K(u_{2s+1} - u_{2s}) . \]

Assuming harmonic solutions

\[ u_{2s+1} = Ae^{i(qx_{2s+1}-\omega t)} , \]

\[ u_{2s} = Be^{i(qx_{2s}-\omega t)} , \]

where \( x_{2s} = x(a+b) \), \( x_{2s+1} = x_{2s} + b \), and \( b \) is the equilibrium distance \((A_1A_2)\), while \( a \) is the distance \((A_2A_1)\), one obtains

\[ (m_2 \omega^2 - K-k)A' + (K+ke^{-i(a+b)})B = 0 , \]

\[ (K+ke^{i(a+b)})A' + (m_1 \omega^2 - K-k)B = 0 , \]

where \( A' = \exp(iqb) \). The eigenfrequencies are obtained from the determinant of the linear set of eqs. (8) resulting in two branches,

\[ \omega^2 = K(1+c) \left( 1 + \Delta \right) / 2M , \]

where \( \Delta = 1 - \frac{8(M_2/m_1 m_2)a(1+a^{-2}(1-c))}{M(M_1 m_2/(m_1+m_2))} \), \( a = k/K \) and \( c = \cos q(a+b) \). In the limit \( q(a+b) \ll 1 \)
one obtains

\[ \omega_+ \approx \sqrt{K(l+\alpha)}/M, \quad (9) \]

\[ \omega_- \approx (M/\sqrt{m_1 m_2})\sqrt{\alpha} q(a+b) = c_s q = \omega_q, \quad (10) \]

where the sound velocity is \( c_s = \sqrt{K/(m_1 + m_2)} \cdot \left(\frac{a+b}{\sqrt{1+\alpha}}\right) \). The ratios of (complex) amplitudes \( A'/B \) are given by

\[ (A'/B)_- \approx 1 + i a q(a+b)(1+\alpha)^{-1} \quad (11) \]

\[ (A'/B)_+ \approx \frac{m_1}{m_2} \left[ 1 + i a q(a+b)(1+\alpha)^{-1} \right] \quad (12) \]

for \( \omega = \omega_- \) and \( \omega = \omega_+ \), respectively, as one can see by replacing eq. (9) or (10) in eqs. (8). Noting that \( u_{2s+1} \) and \( u_{2s} \) are the real parts of the right side of eqs. (7), one obtains, for \( q(a+b) \ll 1 \),

\[ \left[ (u_{2s+1} - u_{2s})/B \right]_+ \approx -(1+\frac{m_1}{m_2}) \cos(qx_{2s} - \omega_+ t) \]

\[ \left[ (u_{2s+1} - u_{2s})/B \right]_- \approx \left(\frac{1}{1+\alpha}\right)^{-1} \sin(qx_{2s} - \omega_- t) q(a+b) \quad (13) \]

\[ \left[ (u_{2s+1} - u_{2s})/B \right]_+ \approx -(1+\frac{m_1}{m_2}) \cos(qx_{2s} - \omega_+ t) \quad (14) \]

for the acoustic and the optical branch, respectively. In eqs. (13) and (14) we have assumed, without loss of generality, that \( B_+ \) and
B_ are real. In eq.(13), note the π/2 phase difference between 
\((u_\nu)_-\) and \((u_{2s}_2)_- = B_\cos(qx_{2s} - \omega t)\); this fact provides the meaning for the imaginary term in eq.(11). Note also in eq.(13) that the internal vibrational coordinate \((u_\nu)_- = (u_{2s+1} - u_{2s})_1\) oscillates not at its "proper" frequency \(\omega_+\), but at \(\omega = \omega_-.\) Using complex variables one can write:

\[
(u_{2s+1} - u_{2s})_1 \approx \frac{iaq}{(1+a)} ((u_{2s})_1 = B_- (u_{2s})_- ,
\]

\[
(u_{2s+1} - u_{2s})_+ \approx -(1 + \frac{m_1}{m_2}) (u_{2s})_+ = B_+ (u_{2s})_+ ,
\]

in other words, it is agreed that for \(\eta(a+b) \ll 1\), the coefficient \(|B_-|\) in eq.(15) is quite small compared to \(|B_+|\) in eq.(16), but this is more than compensated by the inequality \(<(u_{2s})^2>_+ \gg <(u_{2s})^2>_→\) corresponding to the fact that it is extremely easier to excite oscillations at frequency \(\omega = \omega_0 w_\nu\), compared to those for \(\omega = \omega_+\). The last statement results from the expression (5) \(<(u_{2s})^2>_\pm = \frac{1}{2} + n(\omega_\pm)\hbar/(N\omega_\pm)\). Note also that thermal averages of type \(<(u_{2s})_+(u_{2s})_->_→\) are equal to zero because the plus and minus components correspond to different frequencies. The final result from (15) and (16) is that

\[
< (u_{2s+1} - u_{2s})^2 > \gg < (u_{2s+1} - u_{2s})^2 > ,
\]
for $T < \frac{T_D}{T_L}$, corresponding to the dominance of the $T^4$ term over all other contributions to the NOR frequency shift at sufficiently low temperatures.

The above discussion can be formulated most conveniently in the external modes approximation by decoupling the equations for the center of mass motion $u^t = \frac{m_1u_{2s+1} + m_2u_{2s}}{m}$ from those of the other coordinates, as $u^v = u_{2s+1} - u_{2s}$, in the limit $q(a+b) << 1$. Eq. (13) results then as a perturbation. In other words,

$$u^v = (u^v)_+ + (u^v)_-$$  \hspace{1cm} (18)

where $(u^v)_+$ oscillates at its proper natural frequency $\omega_+$, and $(u^v)_-$ represents the induced component oscillating at the frequency $\omega_-$ of the "external field". Noting that $<(u^v)_+(u^v)_-> = 0$, one obtains from eq. (18)

$$<(u^v)^2> = <(u^v)_+^2> + <(u^v)_-^2>$$  \hspace{1cm} (19)

where the first term in the right side contains the $T^4$ dependence and the second term corresponds to the usual exponential Bayer term. The final result may be written in the form

$$v_o - v(T) = A_o + A T^4 \frac{J(x_D)}{J(x)} + \frac{1}{N} \sum_{q \neq 0} B(q) \frac{1}{\hbar \omega_q / KT}$$  \hspace{1cm} (20)
where \( J(x_D) = \int_0^{x_D} x^3(e^x-1)^{-1} dx \), \( x_D = T_D / T \), \( J(\infty) = \frac{6}{n^4} (1/n^4) \approx 6.5 \); \( A_o \) contains the zero-point contributions from all phonon branches, the \( T^4 \) term corresponds to the forced oscillations induced by the acoustic phonons over all lattice coordinates, and the sum over \( \ell \) is to be extended over all non-acoustic branches. \( N \) is the number of unit cells of the solid. It is also important to realize that the Bayer term, as well as the Debye term are both produced by the modulation of the same coordinates, except that they are modulated at different frequencies. Note also, that, in general, one can write \( A = A(\pi \tau) + A(\pi \nu) + A(\nu \nu) + \ldots \), and a similar expression for \( B_\ell(q) \), corresponding to the various librational and vibrational coordinates that may contribute to the EFG. In eq. (20), the dispersion or \( q \)-dependence of the non-acoustic branches is also included, a necessary precaution at least for the lowest branches. The expression for \( J(x_D) \) is also an approximation, in that certain details of the three acoustic branches are not included. For high precision work, a theory convenient for computer calculations has been formulated, with particular emphasis on the lowest external modes. In this way, all calculations and computer programs already available for the external modes approximation may be used.
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REFERENCES

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FIGURE CAPTIONS

Fig.1. (a) Longitudinal acoustic wave modulating vibrational coordinate $u_v$ at frequency $\omega_{qa}$; (b) transversal acoustic wave modulating librational coordinate $\theta$ at frequency $\omega_{qa}$.

Fig.2. Diatomic linear chain model, $A_1$ at site $2s$ and $A_2$ at site $2s+1$. 
LONGIT. ACOUSTIC WAVE

\[ u_v = u_{2s+1} - u_{2s} \]
\[ u_v \propto \exp(i\omega_{q,t}) \]

(b)

\[ \theta \approx (u_{2s+1} - u_{2s})/b \]
\[ \theta \propto \exp(i\omega_{q,t}) \]

FIG. 1