

## $T^4$ Dependence of the Nuclear-Quadrupole Resonance Frequencies in Solids\*

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Nuclear-quadrupole-resonance frequencies are shown to have a  $T^4$  dependence which becomes dominant at sufficiently low temperatures; the mechanism is discussed using a diatomic linear-chain model. 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 nonuniform  $q$ -dependent character of the acoustic branch is shown to induce modulations of the librational and vibrational coordinates at the low frequencies of the acoustic phonons. A Debye term is added to the familiar Bayer expression; both terms are shown to be produced by the modulation of the *same* coordinates, except that they occur at *different* frequencies.

Sixteen years ago Kushida, Benedek, and Bloembergen<sup>1</sup> predicted a term of the form

$$AT^4 \int_0^{T_D/T} \left( \frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx, \quad (1)$$

in addition to the usual Bayer<sup>2</sup> term, for the temperature dependence of the nuclear-quadrupole-resonance (NQR) frequencies in solids. In that paper the above term was succinctly ascribed to Debye waves.  $T_D$  is the Debye temperature.

With the detection<sup>3</sup> of a dominant  $T^4$  dependence at low temperatures ( $T \lesssim 35^\circ\text{K}$ ) in a number of solids, it is necessary to obtain a clearer understanding of the mechanism that gives rise to this term as well as its importance for the correct interpretation of NQR data in the high-temperature region.

A more detailed theory<sup>4</sup> based on the external-modes approximation<sup>5</sup> 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 paper to discuss a simplified model based on the diatomic linear chain in order to display the essential ingredients of the problem.

First of all, the Debye waves, i. e., the translational acoustic phonons, are unable, by themselves, to affect *directly* the electric field gradient (EFG) at the quadrupolar nucleus. This fact is a result of the invariance of the EFG under uniform translations which are the dominant feature of the acoustic vibrations in the long-wavelength limit.<sup>6</sup> The only *direct* effect produced by the translational acoustic lattice vibrations is a kinematic, second-order, relativistic Doppler effect wherein the rf frequency undergoes a shift  $\Delta\nu$  when absorbed by the moving quadrupolar nucleus. The instantaneous Doppler shift<sup>7</sup> is given by

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

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

$$v = \dot{u} = \sum_q \omega_q u_q = \frac{1}{\hbar} \sum_q \hbar\omega_q u_q,$$

where  $u_q$  is the Fourier component of  $u$  of wave-length  $2\pi/q$  and frequency  $\omega_q$ , we find

$$\begin{aligned} \langle v^2 \rangle &= \frac{1}{\hbar^2} \sum_q (\hbar\omega_q)^2 \langle u_q^2 \rangle \\ &= \frac{1}{m} \frac{1}{N} \sum_q \hbar\omega_q \left( \frac{1}{2} + n_q \right) \propto U(T), \end{aligned} \quad (2)$$

where  $\langle u_q^2 \rangle = (\frac{1}{2} + n_q)\hbar/Nm\omega_q$ ,  $m$  being the mass of the unit cell and  $N$  the number of unit cells;  $\hbar\omega_q$  is the acoustic-phonon energy and  $n_q = (e^{\hbar\omega_q/kT} - 1)^{-1}$ . As a result  $(\Delta\nu/\nu)_{\text{Doppler}} \propto \langle v^2 \rangle$  in Eq. (2) and 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  $T < T_D$ ,

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

for a Debye temperature  $T_D = 100^\circ\text{K}$  and  $m$  equal to 20 nucleon masses. Even for  $\nu = 100\text{ MHz}$ , one obtains  $(\Delta\nu)_{\text{Doppler}} < 10^{-7}\text{ kHz}$ , while the observed frequency shifts are of the order of 30 kHz for  $T < 30^\circ\text{K}$ .

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 overwhelming presence of translational acoustic

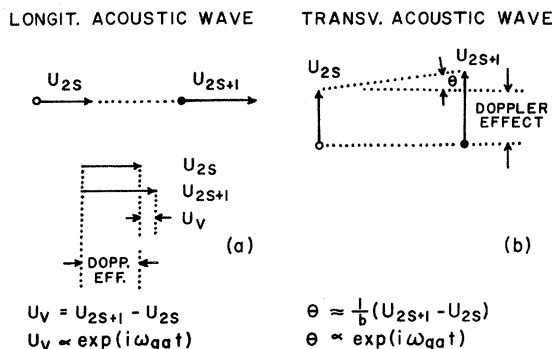


FIG. 1. (a) Longitudinal-acoustic wave modulating vibrational coordinate  $u_v$  at frequency  $\omega_{qa}$ ; (b) transverse-acoustic wave modulating librational coordinate  $\theta$  at frequency  $\omega_{qa}$ . The angular coordinate  $\Theta$  appears in a linear chain, only if transversal motion is allowed, i. e., if the chain is imbedded in two- or three-dimensional space.

phonons of long wavelength at low temperatures  $T \ll T_D$  and (b) the fact that the acoustic phonons present in the solid induce forced librations and vibrations at the very low frequencies  $\omega_{qa}$  of the acoustic branch.

The factor (a) is a well-known result.<sup>8</sup> The ratio of the number of phonons present in the solid belonging to the acoustic and nonacoustic branches is given by  $n_q/n_L \approx (kT/\hbar\omega_{qa})e^{\hbar\omega_L/kT} \gg 1$ , where  $\omega_L$  is the frequency of the lowest, nearly flat, nondispersive, librational, vibrational, or translational optical branch. One can show that the amplitude of the indirect effect (b) is proportional to the small difference in the displacements from one site to the next. In other words, the amplitude of induced libration or vibration is proportional to the small "nonuniform" character present in the translational acoustic branch.

In terms of acoustic waves of momentum  $q$ , one can show that, in the long-wavelength limit,

$$u_{2s+1} - u_{2s} \approx \alpha \sum_q qa(u_{2s})_q \approx \frac{\alpha a}{\hbar c_s} \sum_q \hbar\omega_{qa}(u_{2s})_q, \quad (3)$$

where  $a$  is a lattice distance,  $\alpha$  involves a ratio between two elastic coupling constants,  $u_{2s}(t) = C \cos(qx_{2s} - \omega_{qa}t)$  represents the oscillations of frequency  $\omega_{qa}$  and wave number  $q$ , and  $c_s$  is the velocity of sound in the solid. For the vibrational coordinate  $u_v$ , one can write  $u_v = u_{2s+1} - u_{2s}$  [Fig. 1(a)] or, from Eq. (3),

$$\langle u_v^2 \rangle = \left( \frac{\alpha a}{\hbar c_s} \right)^2 \sum_q (\hbar\omega_{qa})^2 \langle (u_{2s})_q^2 \rangle, \quad (4)$$

which is a result similar to Eq. (2) and results in the same form of temperature dependence as the total vibrational energy of the lattice.

For a librational coordinate  $\theta \approx (1/b)(u_{2s+1} - u_{2s})$  [Fig. 1(b)], one again obtains an expression similar to Eq. (2). The EFG is modulated when the  $\theta$

and  $u_v$  coordinates vary, and these coordinates undergo forced oscillations at the frequencies of the acoustic phonons. The result is that all thermal averages  $\langle \theta^2 \rangle$ ,  $\langle \theta u_v \rangle$ , and  $\langle u_v^2 \rangle$  present a temperature dependence similar to the total vibrational energy  $U(T)$  of the lattice, with a dominant  $T^4$  behavior at sufficiently low temperatures, as confirmed by experiment.<sup>3</sup>

In order to clarify the essential elements for this  $T^4$  dependence, let us consider a simple model, that of a diatomic linear chain (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 quadrupolar 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  $u_{2s} - u_{2s-1}$ , which may be considered as the change of *intermolecular* distance; neglecting more distant molecules, the NQR frequency shift is of the form

$$\Delta\nu = a_{11} \langle (u_{2s+1} - u_{2s})^2 \rangle + a_{12} \langle (u_{2s+1} - u_{2s-1}) \rangle + a_{22} \langle (u_{2s} - u_{2s-1})^2 \rangle + \dots \quad (5)$$

It is important to realize<sup>9</sup> in Eq. (5) that the NQR frequency shifts involve two different and formally independent problems: (a) the quantities  $a_{11}$ ,  $a_{12}$ , and  $a_{22}$  depend exclusively on the *sensitivity* of the EFG tensor  $V$  to the various changing coordinates, and (b) the thermal averages are related to the phonon spectrum, i. e., to the *lattice Hamiltonian*  $H_L$  involving the elastic coupling constants.

Now, each term in Eq. (5) presents the *same*  $T^4$  dependence at low temperature. For this reason let us concentrate our attention on the *intramolecular* distance  $u_v = u_{2s+1} - u_{2s}$ . Considering nearest-neighbor forces only, the equations of motion, for the model of Fig. 2, are given by<sup>8</sup>

$$\begin{aligned} m_2 \ddot{u}_{2s+1} &= K(u_{2s} - u_{2s+1}) + k(u_{2s+2} - u_{2s+1}), \\ m_1 \ddot{u}_{2s} &= k(u_{2s-1} - u_{2s}) + K(u_{2s+1} - u_{2s}). \end{aligned} \quad (6)$$

Assuming harmonic solutions

$$\begin{aligned} u_{2s+1} &= A e^{i(\alpha x_{2s+1} - \omega t)}, \\ u_{2s} &= B e^{i(\alpha x_{2s} - \omega t)}, \end{aligned} \quad (7)$$

where  $x_{2s} = s(a+b)$ ,  $x_{2s+1} = x_{2s} + b$ , and  $b$  is the equilibrium distance  $A_1A_2$ , while  $a$  is the distance

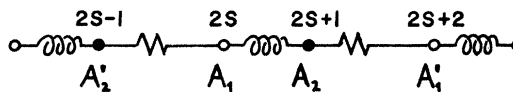


FIG. 2. Diatomic *one-dimensional* (no transversal motion) linear-chain model;  $A_1$  at site  $2s$  and  $A_2$  at site  $2s+1$ .

$A_2' A_1$ , one obtains

$$\begin{aligned} (m_2 \omega^2 - K - k)A' + (K + k e^{i q(a+b)})B &= 0, \\ (K + k e^{-i q(a+b)})A' + (m_1 \omega^2 - K - k)B &= 0, \end{aligned} \quad (8)$$

where  $A' = A e^{i q b}$ . The eigenfrequencies are obtained from the determinant of the linear set of Eqs. (8) resulting in two branches,  $\omega_{\pm}^2 = K(1 + \alpha) \times (1 \pm \sqrt{\Delta})/2M$ , where  $\Delta = 1 - 8(M^2/m_1 m_2)\alpha(1 + \alpha)^{-2} \times (1 - c)$ , with  $M = m_1 m_2 / (m_1 + m_2)$ ,  $\alpha = k/K$ , and  $c = \cos q(a+b)$ . In the limit  $q(a+b) \ll 1$ , one obtains, for the optical frequency  $\omega_+$  and the acoustic frequency  $\omega_-$ ,

$$\omega_+ \approx [K(1 + \alpha)/M]^{1/2}, \quad (9a)$$

$$\omega_- \approx \omega_+ [M^2/(m_1 m_2)]^{1/2} \alpha^{1/2} (1 + \alpha)^{-1} q(a+b) = c_s q = \omega_q, \quad (9b)$$

where the sound velocity is

$$c_s = [k/(m_1 + m_2)(1 + \alpha)]^{1/2} (a+b).$$

The ratios of (complex) amplitudes  $A'/B$  are given by

$$(A'/B)_- \approx 1 + i\alpha(1 + \alpha)^{-1} q(a+b), \quad (10)$$

$$(A'/B)_+ \approx - (m_1/m_2) [1 + i\alpha(1 + \alpha)^{-1} q(a+b)], \quad (11)$$

for  $\omega = \omega_-$  and  $\omega = \omega_+$ , respectively, as one can see by placing Eq. (9a) or (9b) in Eqs. (8). Noting that  $u_{2s+1}$  and  $u_{2s}$  are the real parts of the right-hand sides of Eqs. (7), one obtains, for  $q(a+b) \ll 1$ ,

$$\begin{aligned} [(u_{2s+1} - u_{2s})/B]_- \approx -\alpha(1 + \alpha)^{-1} q(a+b) \\ \times \sin(qx_{2s} - \omega_- t), \end{aligned} \quad (12)$$

$$[(u_{2s+1} - u_{2s})/B]_+ \approx - (1 + m_1/m_2) \cos(qx_{2s} - \omega_+ t) \quad (13)$$

for the acoustic and the optical branches, respectively. In Eqs. (12) and (13) we have assumed, without loss of generality, that  $B_+$  and  $B_-$  are real. In Eq. (12), there is a  $\frac{1}{2}\pi$  phase difference between  $(u_{2s})_-$  and  $(u_{2s})_+ = B_+ \cos(qx_{2s} - \omega_+ t)$ ; this fact provides the meaning for the imaginary term in Eq. (10). It can be noted also in Eq. (12) that the internal vibrational coordinate  $(u_{2s+1} - u_{2s})_-$  oscillates not at its "proper" frequency  $\omega_+$ , but at  $\omega = \omega_-$ . Introducing the complex factors  $\beta_{\pm}$ , we write Eqs. (12) and (13) in the form

$$(u_{2s+1} - u_{2s})_- \approx i\alpha(1 + \alpha)^{-1} q(a+b) (u_{2s})_- = \beta_- (u_{2s})_-, \quad (14)$$

$$(u_{2s+1} - u_{2s})_+ \approx - (1 + m_1/m_2) (u_{2s})_+ = \beta_+ (u_{2s})_+. \quad (15)$$

It is seen that for  $q(a+b) \ll 1$ , the coefficient  $|\beta_-|$  in Eq. (14) is quite small compared to  $|\beta_+|$  in Eq. (15), but this is more than compensated by the inequality  $\langle (u_{2s})_-^2 \rangle \gg \langle (u_{2s})_+^2 \rangle$ , corresponding to the fact that it is very much easier to excite oscillations at frequency  $\omega_- = \omega_{qa}$  than at  $\omega$ . The last statement results from the expression<sup>6</sup>  $\langle (u_{2s})_{\pm}^2 \rangle$

$= [\frac{1}{2} + n(\omega_{\pm})] \hbar / Nm\omega_{\pm}$ . Note also that thermal averages of the type  $\langle (u_{2s})_+ (u_{2s})_- \rangle$  are equal to zero because the plus and minus components correspond to different frequencies. The final result from (14) and (15) is that the temperature-dependent parts obey

$$\langle (u_{2s+1} - u_{2s})_-^2 \rangle \gg \langle (u_{2s+1} - u_{2s})_+^2 \rangle \quad (16)$$

for  $T \ll T_D$  and  $T \ll \hbar\omega_L/k$ , corresponding to the dominance of the  $T^4$  term over all other contributions to the NQR frequency shift at sufficiently low temperatures.

The above discussion can be formulated<sup>4</sup> most conveniently in the external-modes approximation by decoupling the equations for the center-of-mass motion  $u_s^{\pm} = (m_1 u_{2s+1} + m_2 u_{2s})/m$  from those of the other coordinates, as, for example,  $u_s^{\nu} = u_{2s+1} - u_{2s}$ , in the limit  $q(a+b) \ll 1$ . Equation (12) results then as a perturbation. In other words,

$$u^{\nu} = (u^{\nu})_+ + (u^{\nu})_-, \quad (17)$$

where  $(u^{\nu})_+$  oscillates at its proper natural frequency  $\omega_+$ , and  $(u^{\nu})_-$  represents the induced component oscillating at the frequency  $\omega_-$  of the "external field." Noting that  $\langle (u^{\nu})_+ (u^{\nu})_- \rangle = 0$ , one obtains from Eq. (17),

$$\langle (u^{\nu})^2 \rangle = \langle (u^{\nu})_-^2 \rangle + \langle (u^{\nu})_+^2 \rangle, \quad (18)$$

where the first term on the right-hand 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

$$\begin{aligned} -(\nu - \nu_0) = A_0 + A T^4 \frac{J(x_D)}{J(\infty)} \\ + \frac{1}{N} \sum_{lq} B_l(q) \frac{1}{e^{\hbar\omega_q l / kT} - 1}, \end{aligned} \quad (19)$$

where

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

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

$A_0$  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  $l$  is to be extended over all nonacoustic branches.  $N$  is the number of unit cells in the solid. It is important to realize that the Bayer term and the Debye term are both produced by the modulation of the *same* coordinates, except that they are modulated at *different* frequencies. In Eq. (19), the dispersion or  $q$  dependence of the nonacoustic branches has been included, a necessary precaution at least for the lowest branches. The expres-

sion for  $J(x_D)$  is an approximation, in that certain details of the three acoustic branches are not included. For high-precision work a theory<sup>4</sup> 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<sup>5</sup> may be used.

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## Defects in Neutron-Irradiated Strontium Titanate: $Ti^{3+}$ "Off Center" on a $Sr^{2+}$ Site

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Nominally pure  $SrTiO_3$  crystals show, after irradiation with fast neutrons, paramagnetic-resonance (EPR) spectra arising from  $Ti^{3+}$  ions on  $Sr^{2+}$  sites. Because of its smaller radius, the  $Ti^{3+}$  sits "off center". In the tetragonal low-temperature phase of  $SrTiO_3$  ( $T < T_c \approx 105$  K) it moves towards one of the twelve surrounding oxygen ions roughly  $0.03 \text{ \AA}$  in a direction perpendicular to the domain axis. This is proved by the response of the EPR spectra to the application of external electric fields. For  $T > T_c$  simultaneously another  $Ti^{3+}$  spectrum is seen, which results from a partial averaging of the low-temperature spectrum. The coexistence of both types of spectra is attributed to the critical dynamics of the fluctuations of the order parameter  $\varphi$  near  $T_c$ . For  $T = (T_c + 4) \pm 0.5$  K a frequency spread of  $\Delta\nu = 3.5 \times 10^8$  Hz is obtained corresponding approximately to the width of the *central mode*.

### I. INTRODUCTION

In this paper, paramagnetic-resonance (EPR) spectra of a  $Ti^{3+}$  center are reported which are observed after fast-neutron irradiation of undoped "pure"  $SrTiO_3$ . They are identical to those previously observed by van Engelen and Henning<sup>1</sup> in one sample of reduced  $SrTiO_3$ . These authors, however, did not give a definite interpretation of the spectra. We show here that they result from a  $Ti^{3+}$  ion on a  $Sr^{2+}$  site. The titanium ion is not found at an ideal lattice position but is moved off center towards one of the 12 surrounding oxygen ions. The assignment of the center was accom-

plished by investigating the spectra above and below the cubic-to-tetragonal phase transition of  $SrTiO_3$  at  $T_c \approx 105 \text{ K}$ <sup>2</sup> and by observing the change of the EPR spectra when external electric fields were applied.

It is seen that the orthorhombicity of the centers observed in the tetragonal low-temperature phase is caused by the tilting<sup>2</sup> of the oxygen octahedra. However, in contrast to the response of all other paramagnetic centers in  $SrTiO_3$ , this orthorhombicity does not follow the order parameter  $\varphi$  but changes to zero at  $T_c$  in a rather abrupt manner. This is a consequence of the more indirect coupling between center and lattice and gives the opportunity