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Uniaxial stress dependence of the nuclear quadrupole resonance frequency of ^{35}Cl in NaClO_3

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Abstract. Measurements of the NQR frequency of the ^{35}Cl nucleus in single crystals of sodium chlorate were made as a function of isothermal uniaxial stress along the (100), (110) and (111) crystalline directions, in the pressure range 0–4 MPa, at several temperatures around room temperature. A linear and directional behaviour is observed.

A model is developed in order to obtain the linear terms of the static and dynamic contributions to the total variation in the electric field gradient (EFG) at the nucleus site. Also an averaged Grüneisen parameter of the rotational modes of ClO_3^- was estimated; this was found to have a negative value at room temperature. From the results it is inferred that the static and dynamic contributions have the same order of magnitude. The self-energy term due to anharmonicity of the rotational modes was obtained at room temperature. The result is a positive value of the same order of magnitude as the thermal strain contribution.

1. Introduction

When the crystalline lattice undergoes elastic strains, such as those originating in external stress or thermal expansion, the crystal field is perturbed and, as a consequence, the electric field gradient (EFG) at the resonant nuclei suffers two effects essentially: one is the change in the rigid-lattice EFG (static contribution); the other is a change in the thermal average due to the perturbation of the force constants (dynamic contribution). Nuclear quadrupole resonance (NQR) is an adequate technique for investigating these changes, because the resonant nuclei act as microscopic probes which are able to detect very small alterations in their environment.

In many problems in which the NQR frequency behaviour due to isobaric heating is studied, it becomes necessary to make a previous estimate of the influence of thermal expansion, because it is responsible for an important portion of the total variation with temperature at constant pressure.

Usually, the thermal expansion effect is estimated through experiments involving high hydrostatic pressures (Kushida *et al* 1956), but this kind of experimental procedure becomes inadequate when dealing with anisotropic media because both the thermal expansion and the compressibility coefficients are not scalars. Uniaxial stress experiments instead should have the advantage of giving sufficiently detailed information in order to take account of the crystalline anisotropy. Also, when using a high-pressure scale, only global behaviour can be observed, ruling out the detection of interesting local

features. Therefore the experimental method that we employed in the present work is the application of a small uniaxial isothermal stress.

In this paper we propose a method for determining the linear terms of the static and dynamic contributions to the total variation in the EFG at the resonant nuclei site due to a small homogeneous deformation. In the framework of a pseudo-harmonic approach, we start from the Bayer–Kushida expression for $\nu_Q(T)$ at constant configuration (Kushida 1955) and introduce a strain dependence of both the EFG of the rigid lattice and the external vibrational frequencies through power expansions in the strain tensor; the frequencies are also assumed to be temperature dependent at constant configuration (self-energy). By assuming a linear dependence with the strain tensor of these two quantities for small strains, we deduce expressions for the first-order derivative of ν_Q with respect to the stress exerted along an arbitrary direction and its temperature dependence for a small temperature range around room temperature.

In order to illustrate our procedure we applied it to sodium chlorate. This compound exhibits some interesting properties from the viewpoint of NQR. The spin–lattice relaxation time of ^{35}Cl has an exponential behaviour above 330 K and $\nu_Q(T)$ at zero pressure deviates from the Bayer–Brown model at high temperatures (Kasprzac and Pietrzak 1982). Also, the dielectric constant behaviour at low frequencies shows a Debye-type relaxation, which has been accounted for by assuming that the chlorine atom reorients in a double-well potential (Prasad Rao *et al* 1974).

By measuring ν_Q with an isothermal uniaxial stress exerted along the (100), (110) and (111) crystalline directions at several temperatures near room temperature, we determined the linear term of the dynamic contribution; from these data we estimated a Grüneisen parameter averaged over the rotational modes which affect the quadrupole coupling. Also we determined the linear terms associated with the static contribution.

From our results we conclude that the changes in both the vibrational spectra and the EFG of the rigid lattice, due to small deformations of the lattice, have similar influences on the NQR frequency at room temperature.

The thermal strain contribution to the averaged temperature coefficient at constant pressure of the rotational frequencies was also deduced. This result, together with the temperature coefficient at constant pressure observed by Raman spectroscopy (Prasad Rao *et al* 1974), allowed us to estimate the self-energy term at room temperature; this was found to be positive and of the same order of magnitude as the thermal strain contribution.

2. Theory

The model developed by Bayer (1951) and later generalized by Kushida (1955) for the temperature dependence of the NQR frequency ν_Q at constant crystalline configuration, when the EFG has cylindrical symmetry, is condensed in the equation

$$\nu_Q(T) = \nu_0 \left[1 - \frac{3}{2} \sum_j \frac{A_j}{\omega_j} \coth \left(\frac{\hbar \omega_j}{2k_B T} \right) \right] \quad (1)$$

where ν_0 represents the NQR frequency corresponding to a fictitious rigid lattice; ω_j is the frequency of the j th normal mode, all the modes which have an influence on the EFG averaging being included. The A_j are coefficients originating in a normal-mode expansion of the magnitude of the maximum principal axis of the EFG and the angle of inclination

of the maximum principal axis relative to its equilibrium direction. When the resonant nucleus belongs to a rigid molecule or ion, on the assumption that the torsional modes do not couple with translational modes, then A_j^{-1} can be interpreted as the moment of inertia of the j th rotatory mode.

Because of the anisotropy of the lattice, the appropriate thermodynamic variables for describing the state of a strained crystal are, in the absence of electric or magnetic fields, the temperature and the strain and stress tensors, both tensors being of second rank and symmetric. Following Callen (1960), the strain tensor ε_k , $k = 1-6$, is defined as

$$\varepsilon_k = \begin{cases} V_0 \varepsilon_{ii} & k = \{1, 2, 3\} \\ 2V_0 \varepsilon_{ij} & k = \{4, 5, 6\} \end{cases}$$

where ε_{ii} is the fractional change in length of an element initially parallel to x_i ($i = x, y, z$). Similarly, $2\varepsilon_{ij}$ is the change in the angle between two elements initially along the x_i and x_j axes. V_0 represents the volume of the unstrained crystal.

The stress tensor σ_k , $k = 1-6$, is defined as

$$\sigma_k = \begin{cases} \sigma_{ii} & k = \{1, 2, 3\} \\ \sigma_{ij} & k = \{4, 5, 6\} \end{cases}$$

where σ_{ij} represents the j th component of the force which acts on a unit x_i -directed surface.

The NQR frequency can be considered as a thermodynamic function of the temperature and the strain tensor. The temperature dependence arises explicitly from the statistical average but also indirectly from the constant-configuration dependence of the phonon frequencies (self-energy). The strain dependence arises because of changes in ν_0 and also from the phonon frequencies. Taking into account all these, equation (1) can be rewritten as

$$\nu_Q(T, \varepsilon_k) = \nu_0(\varepsilon_k)F[T, \omega(T, \varepsilon_k)]$$

where

$$F[T, \omega(\varepsilon_k, T)] = 1 - \frac{3}{2}\hbar \sum_j \frac{A_j}{\omega_j(\varepsilon_k, T)} \coth\left(\frac{\hbar\omega_j(\varepsilon_k, T)}{2k_B T}\right). \tag{2}$$

On the basis of previous experimental results on *p*-dichlorobenzene (Zamar and Brunetti 1988), we assume a linear dependence of ν_Q on strain for small stress. Therefore, for an arbitrary γ th configuration of strain, the variation at constant temperature could be expressed as

$$\Delta\nu_Q^{(\gamma)} = \sum_{k=1}^6 Q_k \varepsilon_k^{(\gamma)} \tag{3}$$

where $Q_k = (\partial\nu_Q/\partial\varepsilon_k)_{\varepsilon=0}$ is a constant second-rank symmetrical tensor, which includes the static and the dynamic contributions:

$$Q_k = Q_k^d + Q_k^s \tag{4}$$

$$Q_k^d = \nu_0(\varepsilon = 0)(\partial F/\partial\varepsilon_k)_{\varepsilon=0} \tag{5}$$

$$Q_k^s = F(T, \varepsilon = 0)(\partial\nu_0/\partial\varepsilon_k)_{\varepsilon=0}.$$

2.1. The dynamic contribution

In the presence of a given strain configuration, the force constants of the crystal are perturbed and this leads to a distortion of the vibrational spectra with respect to the

unstrained state. In the case of small stresses, we assume that the only changes which occur are the shifts of the central peaks of the external phonons.

At the γ th configuration of strain, the relative variation in the frequency of the i th external mode is

$$\frac{\Delta\omega_i}{\omega_i} = \sum_k V_k^{(i)} \varepsilon_k^{(\gamma)} + \sum_{mn} W_{mn}^{(i)} \varepsilon_m^{(\gamma)} \varepsilon_n^{(\gamma)} + \dots \quad (6)$$

The quantities $V_k^{(i)} = (1/\omega_i)(\partial\omega_i/\partial\varepsilon_k)_{\varepsilon=0}$, $W_{mn}^{(i)} = (1/\omega_i)(\partial^2\omega_i/\partial\varepsilon_m\partial\varepsilon_n)_{\varepsilon=0}$, etc, are the Grüneisen tensors of first order, second order, etc. We assign $\varepsilon = 0$ to a reference state, e.g. $T = 300$ K and atmospheric pressure. The observed linear behaviour of the NQR frequency with stress suggests a linear dependence of the vibrational frequencies (Zamar and Brunetti 1988). Then, the dynamic contribution in the high-temperature regime ($\hbar\omega_i/2k_B T \leq 1$) is

$$Q_k^d = 3\nu_0 k_B T \sum_i \frac{A_i}{\omega_i^2} V_k^{(i)}. \quad (7)$$

It can be shown (Timan 1966) that, in those crystals with cubic, orthorhombic, hexagonal and tetragonal symmetries, there is no influence of the off-diagonal elements of the strain tensor on the vibrational frequencies, to first order in strain. Therefore, for these kinds of crystals, the dynamic contribution to the NQR frequency variation from angular dilatations is null, at this order of perturbation.

2.2. The static contribution

Following similar reasoning as for the dynamic contribution, we also start to expand ν_0 in a power series of the strain tensor, again keeping just the linear terms because of the observed linear behaviour of the NQR frequency in the presence of small stresses:

$$\nu_0(\varepsilon^{(\gamma)}) = \nu_0(\varepsilon = 0) + (\partial\nu_0/\partial\varepsilon_k)_{\varepsilon=0} \varepsilon_k^{(\gamma)}. \quad (8)$$

Again, $\varepsilon = 0$ represents the state corresponding to $T = 300$ K and atmospheric pressure.

2.3. Stress dependence

As we stated above, the thermodynamic state of the crystal could be described in terms of the temperature and the stress and strain tensors. These magnitudes are interrelated by state equations such as

$$\varepsilon_k = \varepsilon_k(T, \sigma_l) \quad l = 1-6. \quad (9)$$

With $p = |\mathbf{p}|$ as the uniaxial compression, the derivative of ν_0 with respect to the stress is represented by

$$\left(\frac{\partial\nu_0}{\partial p}\right)_T^{(\gamma)} = \sum_{kl} (Q_k^d + Q_k^s) S_{kl} \left(\frac{\partial\sigma_l}{\partial p}\right)^{(\gamma)} \quad (10)$$

where $S_{kl} = (\partial\varepsilon_k/\partial\sigma_l)_T$ are the isothermal elastic constants and $(\partial\sigma_l/\partial p)^{(\gamma)}$ are the geometric coefficients to be determined by imposing the equilibrium condition over the crystal surface in the γ th configuration of stress; Hooke's law was used to obtain equation

(10). Finally we synthesize the linear behaviour of ν_Q with stress at $T = T_0$ through the expression

$$\nu_Q^{(\gamma)}(p, T = T_0) = \nu_Q(p = 0, T = T_0) + (\beta_d^{(\gamma)} + \beta_s^{(\gamma)})p \quad (11)$$

where

$$\beta_d^{(\gamma)} = \sum_{kl} Q_k^d S_{kl} \left(\frac{\partial \sigma_l}{\partial p} \right)^{(\gamma)}$$

$$\beta_s^{(\gamma)} = \sum_{kl} Q_k^s S_{kl} \left(\frac{\partial \sigma_l}{\partial p} \right)^{(\gamma)} \quad (12)$$

with $\beta_s^{(\gamma)} + \beta_d^{(\gamma)}$ being the observed slope of the NQR frequency due to uniaxial stress.

2.4. Temperature dependence of $(\partial \nu_Q / \partial p)_T^{(\gamma)}$

We had assumed that, when the crystalline configuration is slightly distorted from a reference state, the shift occurring in ν_Q is linear and is characterized by the strain-independent tensor Q_k . Then, for a small temperature range around the reference state, the change in the slope with temperature would be mostly due to the explicit dependence of the dynamic contribution Q_k^d (see equation (7)). Then, equation (10) could be condensed as follows:

$$(\partial \nu_Q / \partial p)_T^{(\gamma)} = A^{(\gamma)} T + \beta_s^{(\gamma)} \quad (13)$$

$$A^{(\gamma)} = \frac{\partial \beta_d^{(\gamma)}}{\partial T} = \frac{1}{T} \sum_{kl} Q_k^d S_{kl} \left(\frac{\partial \sigma_l}{\partial p} \right)^{(\gamma)} \quad (14)$$

Combining equations (7) and (14) we find that

$$A^{(\gamma)} = 3\nu_0 k_B \sum_i \frac{A_i}{\omega_i^2} \sum_k \bar{V}_{kl} S_{kl} \left(\frac{\partial \sigma_l}{\partial p} \right)^{(\gamma)} \quad (15)$$

where we defined \bar{V}_k as

$$\bar{V}_k = \sum_i \frac{A_i}{\omega_i^2} \nu_k^{(i)} / \sum_i \frac{A_i}{\omega_i^2} \quad (16)$$

The coefficients \bar{V}_k represent the Grüneisen tensor, averaged over the external modes, with weightings which are proportional to the influence that each mode has on the NQR frequency. Essentially, the k th component of this tensor represents the averaged sensitivity of the torsional modes due to the k th component of the strain tensor.

From the foregoing analysis we conclude that, by measuring $(\partial \nu_Q / \partial p)_T^{(\gamma)}$ as a function of temperature for a set of non-equivalent crystalline directions, it is possible to determine Q_k^d , $A^{(\gamma)}$ and \bar{V}_k .

2.5. The case of NaClO_3

NaClO_3 is cubic, belongs to the $T^4 (P2_13)$ space group and has four formula units per primitive unit cell (Wyckoff 1957). The lattice is ionic, consisting of sodium and chlorate ions. In forming the ClO_3^- group the chlorine atom is in a positive oxidation state and so cannot form ionic bond with the neighbouring Na^+ . This view is supported by the fact

that the distance between the chlorine atom and neighbouring Na^+ is greater than the sum of their ionic radii. The sodium atoms couple ionically with the negatively ionized oxygen atoms of the chlorate group. Therefore it could be roughly considered that the ClO_3^- is suspended in the lattice by the $\text{O}^- - \text{Na}^+$ bonds (Kushida 1955). The Raman spectrum of this crystal exhibits two well separated frequency ranges: a low-frequency region up to 220 cm^{-1} , and a high-frequency region from 480 to 1100 cm^{-1} (Hartwig *et al* 1969). All these features allow us to consider the chlorate ion as having sufficiently strong intraionic forces which justifies the rigid-body approach.

Owing to the cubic symmetry there is only one distinct component of the Q_k^d tensor, which we call the symmetric component $Q_s^d (= Q_1^d = Q_2^d = Q_3^d)$, related to changes in the length of the unit-cell axis. With respect to the static contribution there are two distinct components: the symmetric component $Q_s^s (= Q_1^s = Q_2^s = Q_3^s)$ associated with the diagonal components of the strain tensor and the non-symmetric component $Q_a^s (= Q_4^s = Q_5^s = Q_6^s)$ related to angular dilatations. Equations (13) and (14), specified for (100), (110) and (111) crystalline directions, become

$$(\partial \nu_{\text{O}} / \partial p)_T^{100} = A^{100} T + Q_s^s (2S_2 + S_1) \quad (17)$$

$$(\partial \nu_{\text{O}} / \partial p)_T^{110} = \sqrt{2} A^{100} T + Q_s^s \sqrt{2} (2S_2 + S_1) + (S_3 / \sqrt{2}) Q_a^s \quad (18)$$

$$(\partial \nu_{\text{O}} / \partial p)_T^{111} = \sqrt{3} A^{100} T + Q_s^s \sqrt{3} (2S_2 + S_1) + \sqrt{3} S_3 Q_a^s \quad (19)$$

where

$$A^{100} = \frac{1}{T} Q_s^d (2S_2 + S_1) = 3\nu_0 k_B (2S_2 + S_1) \bar{V}_s \sum_i \frac{A_i}{\omega_i^2} \quad (20)$$

according to equations (14) and (7). In equation (20) we defined $\bar{V}_s = \bar{V}_1 = \bar{V}_2 = \bar{V}_3$. (In this case of cubic symmetry it would also be meaningful to define a volumetric Grüneisen parameter $\mathcal{G} = \bar{V}_s / 3$.) $S_1 = 23.35 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}$, $S_2 = -5.15 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}$ and $S_3 = 85.4 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}$ are the isothermal elastic constants at room temperature, as measured by Mason (1946).

3. Experimental details

Single crystals of NaClO_3 were grown from a solution of high-purity Merck product. The sodium chlorate crystal assumes a cubic form with its faces coinciding with (100), (010) and (001) planes (Mason 1946). Samples were then cut and polished with faces in the (110) and (111) planes. These orientations were confirmed by x-ray diffraction, with an error of less than 5° .

The system designed to exert uniaxial stress has already been described (Zamar *et al* 1983). The reversibility of the process was always checked by observing the ν_{O} -values for increasing and decreasing compression. The NQR lineshape did not show any appreciable change associated with the applied stress and the half-width remained always near 800 Hz during the experiment.

The $\nu_{\text{O}}(p)$ data were obtained with a pulsed spectrometer (Wolfenson *et al* 1989) furnished with a device especially designed to detect very small variations in frequency (Zamar and Brunetti 1988).

The main difficulty that occurred in our experiment was the attainment of the thermal stability of the sample, because the shift of the NQR frequency due to a small stress is of

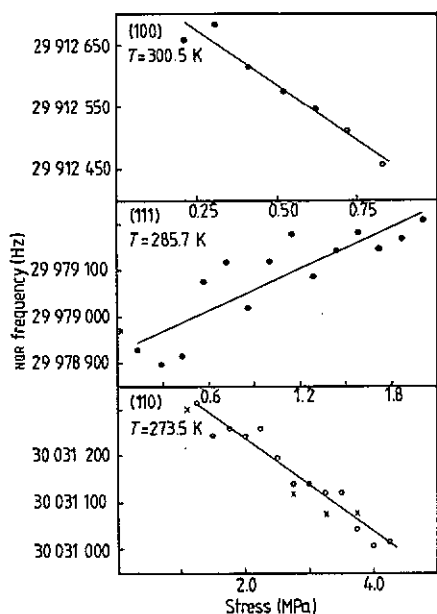


Figure 1. Observed uniaxial isothermal stress dependence of the NQR frequency of ^{35}Cl in NaClO_3 , from 273.5 to 300.5 K, with stress applied along the (100), (110) and (111) crystalline directions: \times , data obtained at zero pressure as measured with decreasing values of stress.

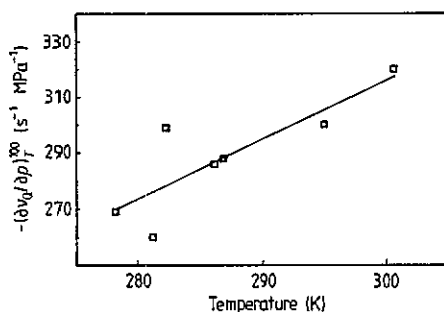


Figure 2. Observed temperature dependence of the slopes associated with the (100) direction, for a small temperature range around room temperature.

the same order of magnitude as those caused by temperature fluctuations within 0.02 K. Therefore, we had to stabilize the sample temperature with a very stable device consisting of a thermal bath whose temperature is controlled by a proportional system with a diode sensor. In this way a temperature stability of better than 0.02 K was achieved. In order to exclude spurious shifts of the NQR frequency caused by any factor other than the homogeneous strain, for each stress value (e.g. the transient heating associated with the isothermal compression, redistributions of defects), we only kept the data which showed a normal distribution around an average, excluding all those which exhibited any other tendency during the short time interval immediately after the application of the stress. By careful inspection of the lineshape we controlled the absence of thermal gradients and inhomogeneities of the strain field.

4. Results and discussion

We measured the dependence of ν_Q on the isothermal uniaxial stress applied along the (100), (110) and (111) crystalline directions of single crystals of NaClO_3 , at several temperatures around room temperature. The results are shown in figures 1 and 2. In agreement with the results obtained previously for *p*-dichlorobenzene (Zamar and Brunetti 1988) a linear behaviour of ν_Q with stress is observed. Also a strong dependence of the slopes on the direction of the applied force is observed. For example, the slopes corresponding to the (100) and (110) directions are negative while the slope associated

with the (111) direction is positive. Our experimental result associated with the (111) direction is consistent with the measurements of Collins and Bloembergen (1964) who also detected a positive shift of the NQR frequency due to a uniaxial stress of 10 kg cm^{-2} at room temperature.

Figure 2 shows the temperature dependence of the slope of $\nu_Q(p)$ for several temperatures, within a small temperature range near room temperature, with the stress applied along the (100) direction. The observed behaviour agrees with that predicted by equation (13). The parameters $A^{100} = -2.15 \pm 0.6 \text{ K}^{-1} \text{ s}^{-1} \text{ MPa}^{-1}$ and $Q_a^s = 2.5 \times 10^7 \pm 4 \times 10^6 \text{ s}^{-1}$ were obtained by fitting the data to this equation. In order to check the internal consistency of our procedure, two independent estimations of Q_a^s were made, by substituting A^{100} and Q_a^s into equations (18) and (19), obtaining the same result: $Q_a^s = 4 \times 10^6 \pm 2 \times 10^6 \text{ s}^{-1}$.

The Grüneisen parameter was estimated from equation (20), obtaining $\bar{V}_s = -21 \pm 6$. Raman data (Prasad Rao *et al* 1974) and the molecular geometry were used to evaluate an averaged torsional frequency and the moment of inertia of the chlorate ion. Consistent with the observed negative slope of $(\partial \nu_Q / \partial p)_T^{100}$ with temperature, a negative value for the Grüneisen parameter was found at room temperature.

Some of the features observed in the NQR frequency of the ^{35}Cl are in contrast with those found in the study of the NQR frequency of Na in NaClO_3 and NaBrO_3 (Early *et al* 1975, Whidden *et al* 1969). In such cubic crystals it was observed that the pressure coefficient of the Na NQR frequency does not depend on temperature or pressure. From our model, this would mean that the only change in ν_Q due to a homogeneous strain arises from the rigid-lattice EFG, whose variation does not depend on temperature and pressure (see equations (13) and (14)). Also, the observed isobaric temperature coefficient of the Na NQR frequency is very small compared with that of Br or Cl in these crystals (Early *et al* 1971, Kushida 1955).

The sources of the EFG at the Na site probably arise, in a large part, from the neighbouring oxygen atoms as well as the nearest chlorate (or bromate) group. As this source is rather extended, it should be expected that the angular displacement of the instantaneous principal axes of the EFG tensor due to thermal motions are averaged out to a considerable extent. This could be the origin of the ineffectiveness of the angular displacement in reducing the NQR frequency with increasing temperature (Whidden *et al* 1969). For the same reason, the dynamic contribution to the pressure coefficient of the NQR frequency would be negligible, because any change in the phonon spectra caused by a homogeneous strain would be screened as a consequence of the small sensitivity of the EFG due to the thermal motion of the source.

However, the EFG at the Cl (or Br) site is mainly due to the intraionic covalent bonds. In this case, the influence of thermal motions of any external source on the principal axis reorientation would be negligible, the rocking motions of the pyramidal group, which would exert a great influence on the instantaneous positions of the principal axes remaining as the principal cause of this reorientation. Therefore, the effectiveness of the angular displacement of the ClO_3^- (or BrO_3^-) group on the averaging of the EFG at the Cl site has to be greater than in the previous case. This reasoning is supported by the experimental fact that the isobaric temperature coefficient of the Cl (Br) NQR frequency is about one order of magnitude greater than that at the Na site. Also, as we had observed, a small perturbation in the phonon spectra, such as that originating in a homogeneous strain, is correlated with the presence of a dynamic contribution which is comparable with the shift in the EFG of the rigid lattice.

Using Brown's (1960) approach for the temperature dependence of the NQR frequency at constant pressure the influence of the thermal strain on the vibrational frequencies are included in the Bayer model for $\nu_Q(T)$ by assuming a phenomenological temperature dependence for the torsional frequency, such as observed in a Raman experiment. In the case of ν_0 , it must be temperature dependent through its strain dependence. In view of a possible strain dependence of Q_k^2 , it could be necessary to include higher-order terms in equation (8) to account for the effects of thermal expansion in a realistic way.

The constant-pressure variation with temperature in the averaged torsional frequency consists of two contributions: one is associated with the thermal expansion; the other is the shift at constant configuration due to phonon-phonon interactions (self-energy). By averaging over the rotational modes as in equation (16), we have

$$\overline{(1/w)(\partial w/\partial T)}_p = \bar{V}_s \alpha + \overline{(1/w)(\partial w/\partial T)}_{\epsilon_s} \quad (21)$$

where $\alpha = 4.3 \times 10^{-5} \text{ K}^{-1}$ is the linear thermal expansion coefficient (Mason 1946). The temperature dependence at constant pressure of the torsional frequencies as measured by Raman spectroscopy is linear, with an averaged slope of $-2 \times 10^{-4} \text{ K}^{-1}$ (Prasad Rao *et al* 1974). By assuming that this feature remains along the Brillouin zone, our estimation for the constant-volume contribution is $\overline{(1/w)(\partial w/\partial T)}_v = 8 \times 10^{-4} \text{ K}^{-1}$. This means that the self-energy term plays an important role in the temperature dependence of the averaged torsional frequency at room temperature.

As a final comment, we think that the small-uniaxial-stress technique can be a simple useful procedure for studying in a detailed way the response of the NQR frequency to changes in the crystal configuration, e.g. in those problems where it is necessary to know the thermal expansion contribution to the total dependence of ν_Q with temperature at a constant pressure.

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