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An NMR study of ^{137}Ba and $^{47,49}\text{Ti}$ in ferroelectric BaTiO_3

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Abstract. A complete NMR characterisation, for the isotopes ^{137}Ba , ^{47}Ti and ^{49}Ti , has been made for a single crystal of BaTiO_3 in the orthorhombic ferroelectric phase at room temperature. The nuclear quadrupole coupling constant and the axially anisotropic component of the chemical shift tensor have been determined for each isotope. In a variable-temperature study up to the Curie point, the nuclear quadrupole coupling constants were found to vary very nearly as the square of the spontaneous polarisation.

1. Introduction

Barium titanate is one of the most technologically important and intensely studied of all piezoelectric and ferroelectric materials. There exists a large body of scientific work on its single-crystal properties and an even larger body of technological work on properties of barium-titanate-based polycrystalline ceramics. (For a selective summary see [1].)

Barium titanate has the idea cubic perovskite structure (figure 1) above its Curie temperature ($T_C = 130^\circ\text{C}$), below which it undergoes, via a first-order transition, a tetragonal distortion along one of the cubic axes to give the ferroelectric phase. The c/a ratio at room temperature is 1.0104, and the atomic displacements from the positions in the cubic structure are in the c direction: $+0.05 \text{ \AA}$ for the Ti, 0.1 \AA for the apical O and 0.006 \AA for the in-plane O. The tetragonal structure persists on cooling down to 3°C whereupon a transformation occurs to a monoclinic structure.

The only NMR measurements to date on barium titanate have been reported for polycrystalline material in the cubic phase above T_C [2]. Sharp resonances were observed for ^{137}Ba and $^{47,49}\text{Ti}$, which disappeared abruptly on cooling to the Curie temperature.

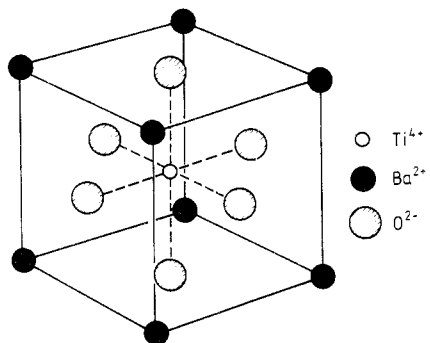


Figure 1. The unit cell for BaTiO_3 in the cubic phase. The room-temperature z -direction atomic displacements in the tetragonal phase are described in the text.

It was reported that the intensity of the ^{137}Ba resonance relative to a $\text{BaCl}_2(\text{aq})$ standard solution indicated that only the central $(\frac{1}{2}, -\frac{1}{2})$ line was present, the inference being that even in the cubic phase a distribution of electric field gradients due to lattice imperfections was sufficient to smear out the first-order satellites through the electric quadrupole interaction.

In the tetragonal phase the Ba and Ti atoms are at sites of axial symmetry (4 mm) where the electric field gradient tensor has zero asymmetry parameter. Note that even in the cubic phase there is cubic point symmetry only at the Ti and Ba sites. At the O site there is an axially symmetric EFG with the axis along either x , y or z . Our attempts to observe the ^{17}O resonance were unsuccessful.

In this work the nuclear quadrupole coupling, e^2qQ/h , and chemical shift anisotropy, σ_a , for ^{137}Ba and $^{47,49}\text{Ti}$ in the tetragonal phase have been determined from single-crystal rotation patterns of the $(\frac{1}{2}, -\frac{1}{2})$ transition frequency. Measurements have also been made of the temperature dependence of the ^{137}Ba and $^{47,49}\text{Ti}$ second-order shifts up to the Curie point, where they vanish abruptly. These shifts are closely proportional to q^2 at the nuclear site in question, where q is the z component of the EFG tensor.

2. Experimental details

The BaTiO_3 crystal used for these measurements was a rectangular specimen, $4 \times 4 \times 7 \text{ mm}^3$, with the tetragonal crystallographic axes parallel to the specimen edges with the long edge parallel to the c axis. Pulsed FT NMR spectra were taken with a Bruker MSL 400 spectrometer at a nominal field of 9.4 T and frequencies of 22.56 MHz for ^{47}Ti ($I = \frac{3}{2}$) and ^{49}Ti ($I = \frac{7}{2}$), and 44.47 MHz for ^{137}Ba ($I = \frac{3}{2}$). Lineshapes were obtained by Fourier transforming the free induction decay after a solid echo sequence, $(\pi/2)_x - \tau - (\pi/2)_y - \tau - aq$. Ringing caused by the piezoelectric properties of the crystal was a problem only for the Ti resonances and was overcome by lengthening the delay τ to 300 s. A delay of 60 μs was adequate for the Ba resonance. Pulse lengths of 2 to 4 μs were used for the $\pi/2$ pulses.

For the rotation patterns, the crystal, initially oriented with $c \parallel B$, was rotated about an a axis, held perpendicular to the magnetic field, and the second-order shift of the $(\frac{1}{2}, -\frac{1}{2})$ resonance, $\nu_{1/2}^{(2)}$, recorded from $\theta = 0^\circ$ to $\theta = 180^\circ$ at intervals of 7.5° , where θ is the angle between the c axis and the magnetic field.

For measurement of the temperature dependence of the second-order shift, the crystal was oriented with the c axis perpendicular to the magnetic field ($\theta = 90^\circ$). In this orientation the lines were relatively sharp, with frequency insensitive to small misorientations. Bearing in mind that the chemical shift tensor will in general be a function of temperature, and that its axial component must go to zero, albeit discontinuously, at T_C , it was necessary to measure both $\nu_{1/2}^{(2)}(90^\circ)$ and $\nu_{1/2}^{(2)}(0^\circ)$ at each temperature. This was fortuitously easy because, on cooling after the first excursion above T_C , the crystal subdivided into tetragonal crystallites with c axes either parallel or perpendicular to the old c axis, because of independent nucleation of tetragonal crystallites with c axes along each of the three cubic axes of the high-temperature phase at the first-order transition. This meant that the 0° and 90° resonances for each isotope were simultaneously present in the spectrum.

Once the coupling constants had been determined at room temperature, an unsuccessful search was made for the first-order $\pm (\frac{1}{2}, \frac{3}{2}) \theta = 0^\circ$ satellites of ^{137}Ba , which gave the best $(\frac{1}{2}, -\frac{1}{2})$ signal intensity of the three isotopes studies here. It seems likely that

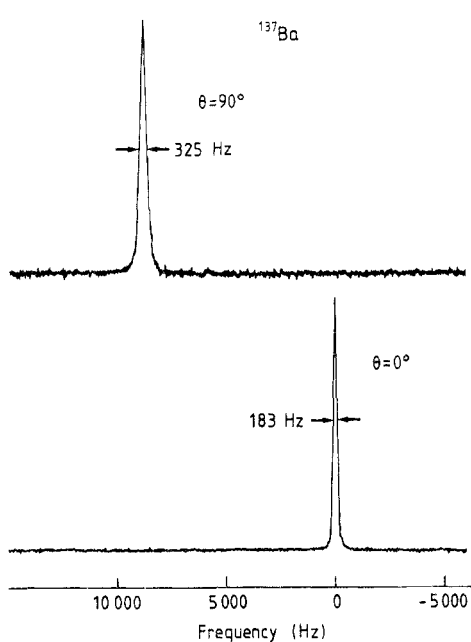


Figure 2. ^{137}Ba lineshapes at $\theta = 0^\circ$ and 90° . The scale zero has arbitrarily been set at the frequency of the $\theta = 0^\circ$ resonance.

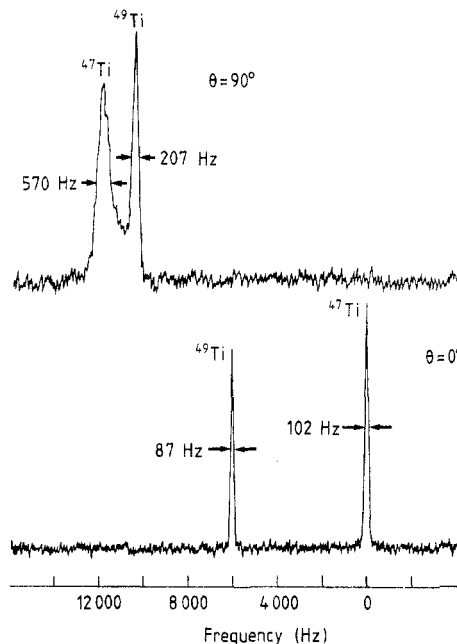


Figure 3. ^{47}Ti and ^{49}Ti lineshapes at $\theta = 0^\circ$ and 90° . The scale zero has arbitrarily been set at the frequency of the ^{47}Ti $\theta = 0^\circ$ resonance.

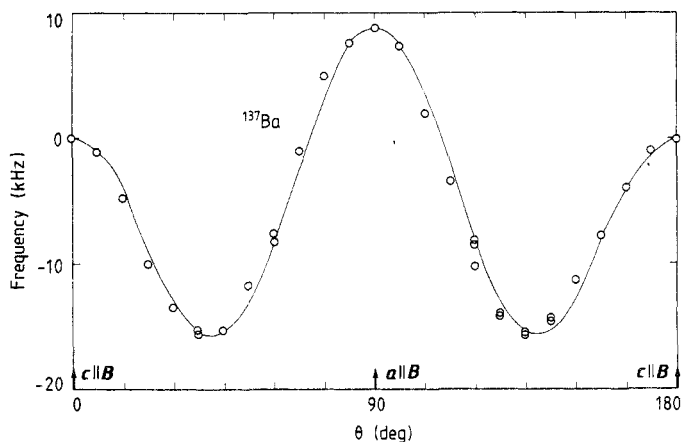


Figure 4. The second-order shift of the ^{137}Ba ($\frac{3}{2}, -\frac{1}{2}$) transition on rotation around a' , with a' perpendicular to B , where a' and a are the two short tetragonal axes. The angle $\theta = 0^\circ$ corresponds to $c \parallel B$. The full curve is obtained by substituting values from table 1 into the expression given in the text.

either random strains or strains due to the presence of ferroelectric domain walls were responsible for broadening these satellites beyond our limit of detectability. However the frequency measurement precision for the central transition was good, as is evident from the lineshapes displayed in figures 2 and 3—much better than the precision to which

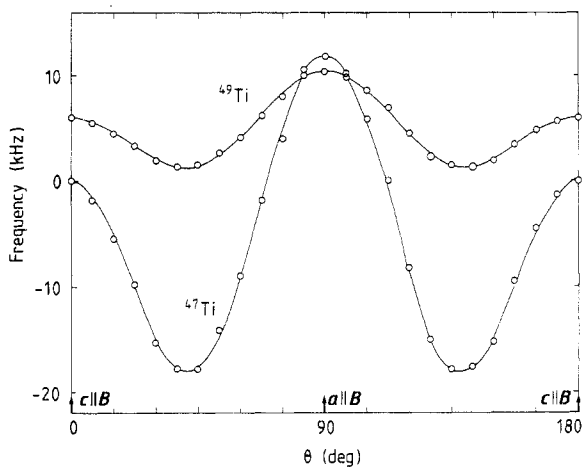


Figure 5. The second-order shift of the ^{47}Ti and ^{49}Ti ($\frac{1}{2}, -\frac{1}{2}$) transitions on rotation around a' , with a' perpendicular to B . The angle $\theta = 0^\circ$ corresponds to $c \parallel B$. The full curve is obtained by substituting values from table 1 into the expression given in the text.

Table 1. Nuclear quadrupole and chemical shift data for ^{137}Ba and $^{47,49}\text{Ti}$ in BaTiO_3 at 296 K.

Nucleus	^{47}Ti	^{49}Ti	^{137}Ba
I	5/2	7/2	3/2
σ_a (ppm)	+42(12)	+40(4)	-1(3)
$ e^2qQ/h $ (MHz)	4.60(3)	3.78(3)	2.90(3)
ν_L (MHz)	22.557	22.563	44.466

the crystal could be oriented ($\pm 1^\circ$) or to which the temperature could be determined at the centre of the RF coil ($\pm 1^\circ\text{K}$).

Relaxation was fast, and no saturation for either Ba or Ti isotopes was observed at room temperature for a pulse sequence repetition rate of 2 Hz. Similarly fast relaxation was noted for the $^{47,49}\text{Ti}$ resonances in TiO_2 (rutile) in [3].

3. Discussion

The rotation patterns for ^{137}Ba and $^{47,49}\text{Ti}$ are displayed in figures 4 and 5. A simple least-squares analysis (employed previously in [4]) was used to extract values of the quadrupole coupling constant and axial component of the chemical shift. The patterns were fitted to the expression [5]

$$\nu_{1/2}^{(2)} = -\nu_0^2 [I(I+1) - \frac{3}{4}](1 - \mu^2)(9\mu^2 - 1)/16\nu_L - \sigma_a \nu_L (3\mu^2 - 1)/2 - \sigma_0 \nu_L$$

where $\nu_0 = 3e^2qQ/2I(2I-1)h$, $\mu = \cos \theta$, ν_L is the Larmor frequency and σ_a is the axially anisotropic component of the chemical shift tensor for which the isotropic component is σ_0 . The results are collected together in table 1.

The ratio of the values of e^2qQ/h for the titanium isotopes yields a ratio for the quadrupole moments $^{49}\text{Q}/^{47}\text{Q} = 0.820(9)$, which is in satisfactory agreement with the value of 0.819(1) obtained from atomic beam data [6].

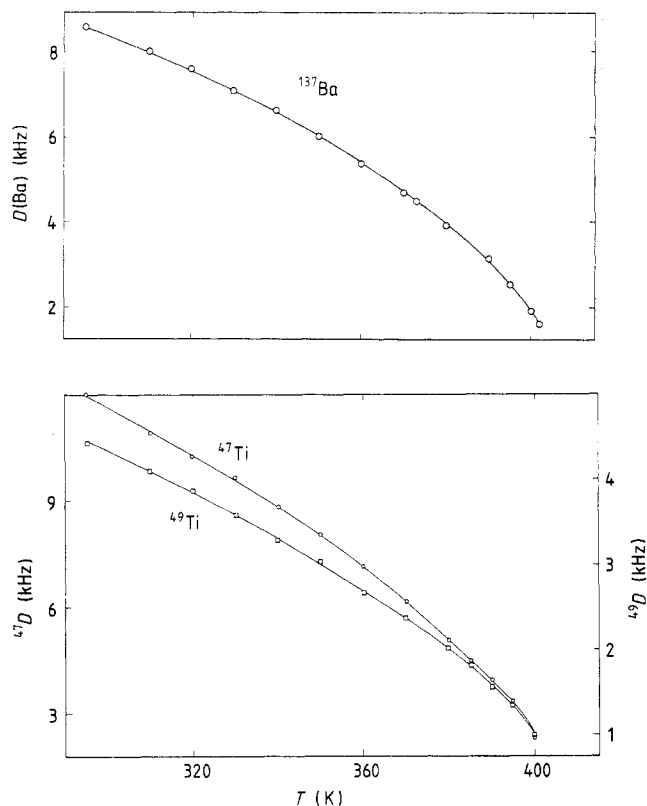


Figure 6. The temperature dependence of the corrected second-order shift $D(\text{Ba})$ for ^{137}Ba , and ^{47}D and ^{49}D for ^{47}Ti and ^{49}Ti respectively. The correction procedure is described in the text. The full curves are guides to the eye.

The Ti coupling constants in BaTiO_3 at room temperature are approximately a factor four smaller than those measured for rutile [3], reflecting the slight tetragonal distortion from cubic symmetry. Analyses of the rotation patterns for ^{47}Ti and ^{49}Ti independently yield the same value of chemical shift anisotropy to within experimental accuracy, namely $\sigma_a = 40$ ppm. The coupling constant for ^{137}Ba is approximately a factor 30 smaller than encountered in more asymmetrical environments, such as in the barium halide dihydrates [7], and again reflects the slight departure from cubic symmetry. Note that the value of σ_a is zero to within experimental error, reflecting the ionicity of the Ba^{2+} bonding in the lattice as compared with the directed, or covalent, bonding between Ti^{4+} and O^{2-} .

The variation of linewidth with angle θ , displayed in figures 2 and 3, deserves some comment. In general there will be both dipolar and quadrupolar contributions to the linewidth. The quadrupolar contribution derives from a distribution of the components of the EFG tensor due to crystal imperfections, such as mosaic structures. Such a distribution is difficult to quantify, but the ratio of the quadrupolar term for ^{47}Ti to that for ^{49}Ti is $\frac{28}{25} (\frac{47}{49} Q)^2 = 3.48$. The quadrupolar term is zero at $\theta = 0^\circ$, so the linewidths observed at this angle should arise from solely dipolar interaction. Assuming Gaussian lines, a Van Vleck second-moment computation yields dipolar linewidths for ^{137}Ba , ^{47}Ti and ^{49}Ti of 108, 62 and 63 Hz, respectively, which underestimate the experimentally observed values. However, if the quadrupolar term for each titanium isotope is estimated by subtracting (in quadrature) the $\theta = 0^\circ$ linewidth from that for $\theta = 90^\circ$, then the ratio

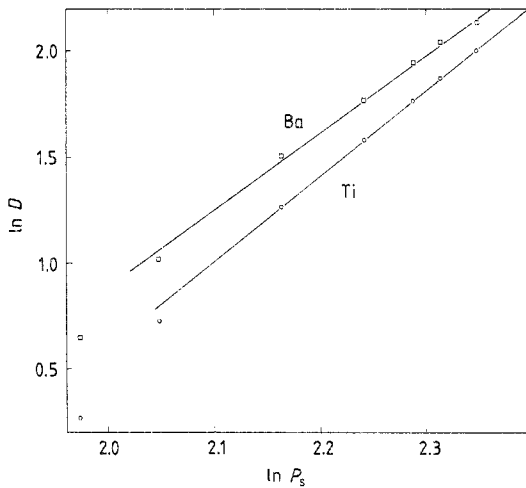


Figure 7. The logarithmic dependence of the corrected second-order shift, D , on spontaneous polarisation, P_s , for ^{137}Ba and ^{47}Ti and ^{49}Ti , where $D = D(\text{Ba})$ or $D(\text{Ti})$, as defined in the text, as appropriate. The straight lines are visual fits to the data away from the transition.

of the ^{47}Ti term to that for the ^{49}Ti term is 3.0, which is in reasonable agreement with the theoretical value above.

The temperature dependence measurements of the second-order shift provide an interesting check on the temperature variation of the spontaneous polarisation, P_s , for which data have been most recently reported in [8]. Dening and Casabella [9] have pointed out that if the atom in question is at a site of inversion symmetry above T_C , and the atoms do not change their bonding state at the ferroelectric transition, then the EFG q should be a quadratic function of P_s . This implies that the second-order shift, corrected for the chemical shift contribution, should be proportional to P_s^4 . For ^{137}Ba , for which σ_a is negligible, a correction to eliminate the temperature dependence of σ_0 was made by subtracting the 0° shift from the 90° shift to give a reduced shift, $D(\text{Ba})$. For each titanium isotope the same subtraction was made and the reduced shift, ^{49}D , for ^{49}Ti was then subtracted from the reduced shift, ^{47}D , for ^{47}Ti to give a quantity, $D(\text{Ti})$, proportional to q^2 , from which the dependence on σ_a had been eliminated. Figure 6 shows plots of $D(\text{Ba})$, ^{47}D and ^{49}D against temperature. Wemple and co-workers [8] measured values for P_s at seven temperatures between room temperature and T_C . Data displayed in log-log form in figure 7 for $D(\text{Ba})$ and $D(\text{Ti})$ against P_s were obtained by graphical interpolation at these temperatures from figure 6. Away from the transition the data may be fitted by straight lines with slopes of 4.00 for titanium and 3.65 for barium. The value for titanium is in good agreement with the expected [9]. For barium the agreement is less satisfactory. In the latter case, since the polarisability of the Ba^{2+} ion is roughly an order of magnitude larger than that for Ti^{4+} , it is possible that the expansion of q in terms of P_s involves higher- (even-) order terms than the second. This would lead to deviations from the simple quadratic behaviour predicted in [9].

The temperature dependence of ν_a was determined from the measurements of $^{47,49}\nu(90)$ and $^{47,49}\nu(0)$ and the derived value of $^{49}Q/^{47}Q$. The shape of the curve was very similar to that for $\nu_Q(T)$, although the scatter in the data points was larger.

Acknowledgments

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