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1990 J. Phys.: Condens. Matter 2 6327

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LETTER TO THE EDITOR

⁹¹Zr nuclear quadrupole coupling in zircon (ZrSiO₄)

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Received 14 May 1990

Abstract. The first measurement of ⁹¹Zr nuclear quadrupole coupling in a solid is reported. The nuclear quadrupole coupling constant (e^2qQ/h) and chemical shift anisotropy (σ_{ax}) for ⁹¹Zr, and the chemical shift anisotropy for ²⁹Si, have been determined for zircon (ZrSiO₄) from high-field NMR single-crystal rotation patterns. A striking variation of ⁹¹Zr linewidth with crystal orientation in the field was observed and explained in terms of local variations in the [001] tetragonal axis orientation due to crystal mosaic structure as well as a distribution of local electric-field gradients due to defects.

Recent characterisation of various forms of zirconium oxides by ¹⁷O MAS NMR [1] has encouraged an examination of the possibility of extending such characterisation to include ⁹¹Zr MAS NMR. For this to be feasible by single-axis MAS NMR, the nuclear quadrupole coupling for ⁹¹Zr ($I = \frac{5}{2}$) would have to be sufficiently small to be effectively spun-out by available rotation frequencies, which are generally of the order 5 kHz. However, no measurement of ⁹¹Zr nuclear quadrupole coupling has previously been reported for any zirconium compound. The difficulty of obtaining solid state ⁹¹Zr NMR powder spectra for anything but rigorously cubic compounds (e.g. ZrZn₂ [2], ZrCo [3] and ZrC [3]) indicates that the coupling is not negligible. The quadrupole moment for ⁹¹Zr (derived from atomic beam resonance methods) is $-0.206 \times 10^{-28} \text{ m}^2$ [4].

Since good quality natural single-crystal zircon is readily available, this was chosen for a determination of what is probably a typical ⁹¹Zr nuclear quadrupole coupling constant when zirconium is bonded to oxygen. Zircon (in fact a double oxide ZrO₂ · SiO₂) has tetragonal symmetry (space group $I4_1/amd$, $Z = 4$) and a structure consisting of linked ZrO₄ and SiO₄ tetrahedra. The crystal used in this investigation was of alluvial origin and pale grey in colour. A high resolution x-ray powder diffraction characterisation of a crushed fragment of the crystal gave the unit cell parameters as $a_0 = 6.5994(12) \text{ \AA}$ and $c_0 = 5.9471(21) \text{ \AA}$ which agreed well with the 1955 NBS entry in the ASTM powder diffraction file.

Since zircon has a unique four-fold axis (the c axis), eta is zero and it is sufficient to perform one rotation about an a axis, with a held perpendicular to the field, to yield a pattern from which the quadrupole coupling and the chemical shift anisotropy can be extracted. Accordingly, the crystal was aligned by x-ray Laue back reflection, and a cylinder 9 mm diameter and 8 mm long, with a [100] axis, was cut from it. This was mounted in a simple rotation stage in the NMR probe and the spectrum recorded at 7.5° intervals.

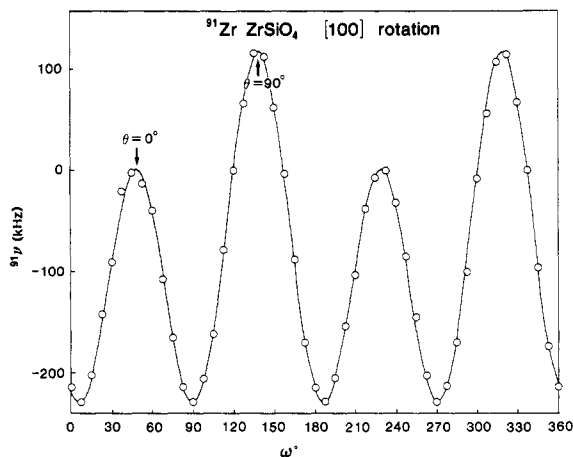


Figure 1. The angular variation of the ^{91}Zr ($\frac{1}{2}$, $-\frac{1}{2}$) transition in zircon. Experimental data are shown as open circles. The full curve is given by equation (1) in the text using the values of ν_Q and σ_a given in table 1. The angle θ between the c axis and the magnetic field is approximately $\omega = 50^\circ$, where ω is the angle read directly from the rotation stage. The frequency scale zero is arbitrary.

The measurements were made at room temperature in a nominal field of 9.4 T with a Bruker MSL 400 spectrometer. For ^{91}Zr ($I = \frac{5}{2}$) a solid echo sequence, $(\pi/2)_x-t-(\pi/2)_y-t-acq$, was used to acquire the line position and shape, since in most orientations the line was broad (~ 5 kHz). The $\pi/2$ pulse length used was $3 \mu\text{s}$ and the echo delay, t , was $10 \mu\text{s}$. For ^{29}Si ($I = \frac{1}{2}$) a simple $\pi/2-acq$ was sufficient because of the considerably narrower line shape due to the absence of quadrupolar effects. The pulse length was $3 \mu\text{s}$. Because the cylindrical sample was rotated about its axis, any demagnetising effect was constant during the rotation. This was only a significant consideration for the ^{29}Si rotation pattern.

For ^{91}Zr the experimental results for angular variation of the frequency of the ($\frac{1}{2}$, $-\frac{1}{2}$) transition and the corresponding linewidth are displayed in figures 1 and 2, respectively. Since it was possible to measure this transition with reasonable precision no serious attempt was made to locate the much broader and weaker satellite resonances. Data could be collected quite rapidly, with a pulse sequence repetition time of two seconds. Saturation was evident if this time was reduced to 0.5 s. Typically between 1000 and 2000 scans were accumulated for each data point.

For ^{29}Si the angular variation of the frequency of the ($\frac{1}{2}$, $-\frac{1}{2}$) transition is shown in figure 3. The linewidth was typically 150 Hz and did not vary significantly during the rotation. The pulse repetition period of 50 s was considerably shorter than the relaxation time. Between 20 and 30 scans were sufficient to define each data point.

For ^{91}Zr ($I = \frac{5}{2}$) the rotation pattern for the ($\frac{1}{2}$, $-\frac{1}{2}$) transition in figure 1 was fitted to the expression [5]

$$\nu_{1/2}^{(2)} = -\nu_Q^2(1 - \mu^2)(9\mu^2 - 1)/2\nu_L - \sigma_a\nu_L(3\mu^2 - 1)/2 - \sigma_0\nu_L \quad (1)$$

where $\mu = \cos \theta$, $\nu_Q = 3e^2qQ/20h$, σ_a and σ_0 are the axially anisotropic and isotropic components respectively of the chemical shift, and ν_L is the Larmor frequency.

For ^{29}Si ($I = \frac{1}{2}$) the rotation pattern in figure 3 was similarly analysed (using only the chemical shift terms) to obtain σ_a .

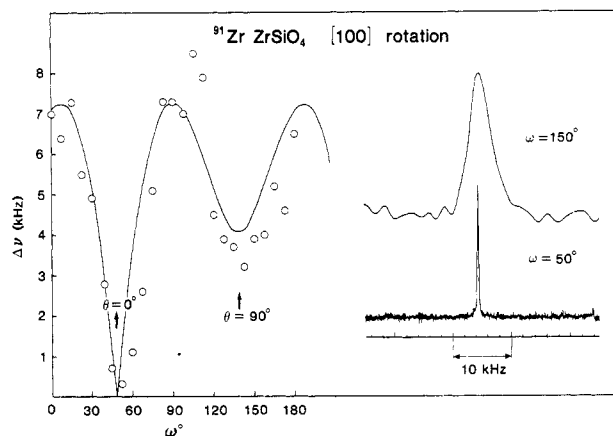


Figure 2. The angular variation of the linewidth of the ^{91}Zr ($\frac{1}{2}, -\frac{1}{2}$) transition in zircon. Experimental data are shown as open circles. The full curve is the fit to the two-term expression described in the text. Observed lineshapes at $\omega = 50^\circ$ and $\omega = 150^\circ$ are shown in the inset.

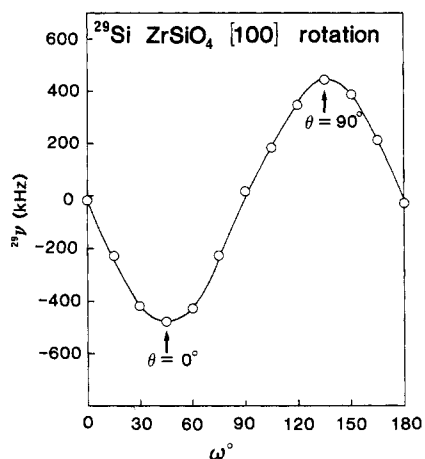


Figure 3. The angular variation of the ^{29}Si ($\frac{1}{2}, -\frac{1}{2}$) transition in zircon. Experimental data are shown as open circles. The full curve is the fit to the chemical shift term only of equation (1). The frequency scale zero is arbitrary.

Table 1

| Isotope | I | e^2qQ/h (MHz) | σ_{ax} (ppm) | ν_L (MHz) |
|------------------|---------------|-----------------|----------------------------|---------------|
| ^{91}Zr | $\frac{3}{2}$ | 20.47 | -169 | 37.33 |
| ^{29}Si | $\frac{1}{2}$ | — | 7.8 | 79.50 |

The results for both isotopes are given in table 1.

The striking angular variation of the ^{91}Zr linewidth exhibited in figure 2(a) can be plausibly modelled with two independent contributions: (i) a distribution of tilt angles of the blocks that comprise the mosaic structure of the crystal, and (ii) a distribution of

the local electric-field gradients due to impurities or crystal defects. The distribution of tilt angles of the local [001] axes about the mean [001] direction may be characterised by an angular width δ_1 , and the EFG distribution characterised by a consequent spread in ν_Q of frequency width δ_2 . The independent contributions due to (i) and (ii) are derived by differentiating equation (1) with respect to θ and ν_Q separately and multiplying by δ_1 and δ_2 respectively. These two contributions are then added in quadrature. A value for δ_1 consistent with the sharpness of the Laue spots is 0.5° . An arbitrary, but not unreasonable value for δ_2 is 50 kHz. Using these values a good qualitative simulation of the linewidth variation is obtained and is displayed in figure 2(b). A neglected and approximately angle-independent contribution is the dipolar linewidth which provides the lower limit when the quadrupolar terms are zero. A Van Vleck second moment estimate for this width is ~ 100 Hz.

It can be reasonably concluded from this measurement of ν_Q that ^{19}Zr single-axis MAS spectra was unlikely to be obtained using currently available rotation frequencies. Furthermore, it seems worth making the general remark that the kind of linewidth versus angle variation displayed in figure 2(a) presents a hazard to quantitative analysis of NMR powder lineshapes.

The relatively large value for σ_a (-183 ppm) for ^{91}Zr may be compared with that obtained in other metal oxide systems where the metal atom has axial symmetry; values of -30 ppm for ^{67}Zn in ZnO [6] and $+40$ ppm for $^{47,49}\text{Ti}$ in BaTiO_3 [7] have been recently reported. The small value for σ_a for ^{29}Si reflects the near tetrahedral symmetry of the SiO_4 molecular grouping.

I am indebted to D Gao for a very careful x-ray Laue characterisation and alignment of two zircon single-crystals, and to D Hay for the x-ray powder determination of the lattice parameters.

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