

Strain-induced inhomogeneous broadening in nuclear quadrupole resonance

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 935

(<http://iopscience.iop.org/0953-8984/1/5/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 17:39

Please note that [terms and conditions apply](#).

Strain-induced inhomogeneous broadening in nuclear quadrupole resonance

C A Schurrer and A H Brunetti

Facultad de Matematica, Astronomia y Fisica, Universidad Nacional de Cordoba,
Cordoba, Laprida 854, 5000 Cordoba, Argentina

Received 3 June 1988

Abstract. An expression for the variation in the inhomogeneous broadening of the nuclear quadrupole resonance linewidth with the temperature was obtained. This model is in good agreement with a linear temperature dependence of the linewidth as is experimentally observed in polycrystalline samples of paradichlorobenzene.

1. Introduction

There is experimental evidence that inhomogeneous broadening occurs in the nuclear quadrupolar resonance (NQR) line owing to the internal stress in molecular polycrystals (Wang 1955). Further, experimental and theoretical work has been carried out on the quadrupolar shift and nuclear magnetic resonance line broadening due to uniaxial external stress and strains generated by defects (Kanert and Mehring 1971). When stresses are applied to single crystals, it is possible to obtain some information about the crystalline structure but, in the presence of a stochastic distribution of strains in a polycrystal, no information in principle can be determined.

In an excellent review paper, Stoneham (1969) presents in a general form the theories used to solve problems of inhomogeneous broadening. Using their basic ideas, we apply that formalism to analyse the temperature dependence of the inhomogeneous broadening of the NQR line arising from the internal stress originating from the anisotropic thermal dilatation coefficient and subgrain boundary ties.

In a subsequent comparison of the theoretical results with the experimental data, we analyse the agreement between these.

2. Theory

The temperature dependence of the NQR frequency can be expressed as (Das and Hahn 1958)

$$\nu(T) = \nu_0 \left[1 - \frac{3}{2} \hbar \sum_i \frac{A_i}{\omega_i} \left(\frac{1}{2} + \frac{1}{\exp x - 1} \right) \right]$$

where T is the temperature, $x = \hbar\omega_i/kT$, ν_0 is the quadrupolar frequency in a stationary

molecule, ω_i is the frequency and A_i is a quantity related to an equivalent moment of inertia of the i th normal mode.

The internal stress in the crystal changes the inter-molecular distance; thus a NQR frequency shift $\Delta\nu$ can occur owing to changes in the static contribution ν_0 and shifts in the librational frequency ω_i . Then, by supposing that $\Delta\omega_i/\omega_i = \Delta\omega/\omega$ for all the external modes, it is easy to see that

$$\Delta\nu(\sigma_1, \dots, \sigma_6) = \nu_0 \sum_i \sum_k \left(\frac{1}{\nu_0} \frac{\partial \nu_0}{\partial u_k} + g(T) \frac{1}{\omega} \frac{\partial \omega}{\partial u_k} \right) S_{ki} \sigma_i \quad k, i = 1, \dots, 6$$

where σ_i is the strain tensor, S_{ki} is the elastic tensor, u_k is the deformation tensor and

$$g(T) = \frac{3}{2} \hbar \sum_i \frac{A_i}{\omega_i} \left(\frac{1}{2} + \frac{1}{\exp x - 1} + \frac{x \exp x}{(\exp x - 1)^2} \right).$$

On the assumption that there is a stochastic distribution in the values of the strain components σ_i , an inhomogeneous broadening of the NQR lineshape results:

$$I(\omega) = \frac{1}{2\pi} \int d\sigma_1, \dots, d\sigma_6 P(\sigma_1, \dots, \sigma_6) \delta(\omega - \Delta\nu(\sigma_1, \dots, \sigma_6)). \quad (1)$$

For simplicity, it is assumed that the joint probability density is separable into products of probability distribution of individual strain components, i.e.

$$P(\sigma_1, \dots, \sigma_6) = P(\sigma_1) \dots P(\sigma_6).$$

Since we are interested in the changes (with temperature) of width and not in the shape of the resonance line, a Lorentzian density is proposed (a Gaussian density leads, likewise, to a similar qualitative behaviour):

$$P(\sigma_i) = \delta/\pi(\sigma_i^2 + \delta^2).$$

By inserting this into (1), one obtains

$$I(\omega) = A/\pi(\omega^2 + A^2)$$

where

$$A = \nu_0 \delta \left| \sum_i \sum_k \left(\frac{1}{\nu_0} \frac{\partial \nu_0}{\partial u_k} + g(T) \frac{1}{\omega} \frac{\partial \omega}{\partial u_k} \right) S_{ki} \right|.$$

$\gamma_k = -(1/\omega)(\partial\omega/\partial u_k)$ is the Grüneisen constant associated with the k th component of the deformation tensor. In this way, A can be expressed as

$$A = \nu_0 \delta \left| \sum_i \sum_k \left(\frac{1}{\nu} \frac{\partial \nu_0}{\partial u_k} - g(T) \gamma_k \right) S_{ki} \right|.$$

An expression for δ cannot be obtained in a general form because the strain distribution depends on the material and the particular grain boundary model. However, in a simple model, it can be assumed that the thermal dilatation constant has different values on both sides of the grain boundary plane (within this simplification, only the thermal expansion in a direction which lies on a plane parallel to this plane will be relevant). If α is a representative value of this difference, the deformation tensor becomes proportional to $T_0 - T$ where T_0 is the solidification temperature. Then, the

more general form of a strain distribution width is

$$\delta = c(T_0 - T)$$

where c is temperature independent and is constant within the elastic range; c describes the average 'strength' of the deformation tensor in the whole crystal. Thus

$$A = c\nu_0(T_0 - T) \left| \sum_i \sum_k \frac{1}{\nu_0} \frac{\partial \nu_0}{\partial u_k} S_{ki} - \sum_i \sum_k g(T) \gamma_k S_{ki} \right|. \quad (2)$$

In the case where the second sum can be neglected, a linear temperature dependence of the inhomogeneous broadening is predicted. Further, when ν_0 falls to zero (as in cubic lattices) (2) is reduced to (Shulman *et al* 1957)

$$A = \delta \left| \sum_i \sum_k \frac{\partial \nu_0}{\partial u_k} S_{ki} \right|.$$

3. Experimental details

In this work, we analyse the linewidths in paradichlorobenzene samples (in both single crystals and polycrystals). We chose this compound because its thermal expansion tensor shows marked anisotropy.

The samples were obtained from commercial paradichlorobenzene purified by repeated recrystallisation. Single crystals were grown by two methods: by sublimation

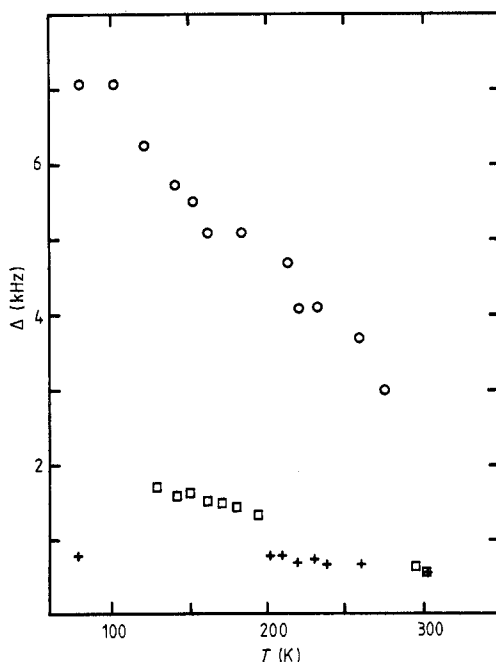


Figure 1. Temperature dependence of the linewidth in paradichlorobenzene samples obtained by different methods: +, single crystals obtained by sublimation; □, single crystals obtained by the Bridgman method; ○, polycrystals in a ceramic matrix.

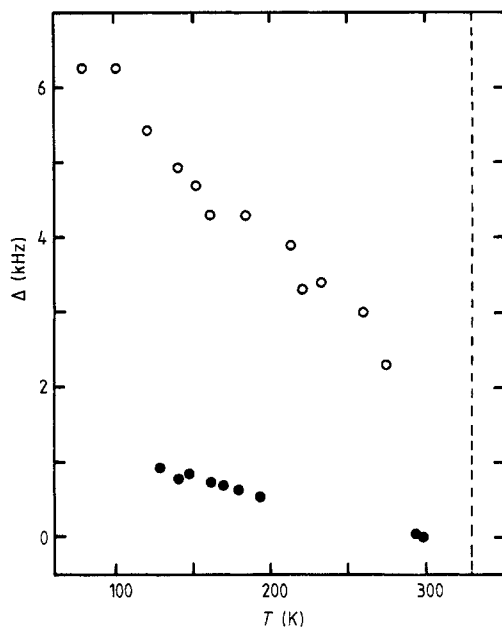


Figure 2. Temperature dependence of inhomogeneous broadening in paradichlorobenzene samples obtained by the Bridgman method (●) and polycrystals in a ceramic matrix (○). The broken line indicates T_0 .

and by the Bridgman method. Polycrystals were also obtained by two methods: the first method allows a liquid sample to solidify at room temperature and the second method is by absorbing liquid paradichlorobenzene in a ceramic matrix with a mean diameter pore of $5 \mu\text{m}$ and leaving it to solidify at room temperature. The linewidths were measured by fast Fourier transform spectroscopy with a Nicolet 4094 B instrument which had a resolution of 100 Hz.

The measured data are plotted in figure 1. The linewidths obtained for polycrystals grown by the first method and single crystals obtained by the Bridgman method have the same temperature dependences; therefore, only the latter are depicted in this figure.

The inhomogeneous broadening is shown in figure 2. These values were obtained by assuming that the linewidth for single crystals grown by sublimation is completely due to homogeneous broadening.

The data from single crystals obtained by sublimation and from polycrystals in a ceramic matrix are the same (within experimental error) on increasing or decreasing the temperature between 77 and 300 K. For the other polycrystals and single crystals, this reversibility range was reduced from 130 to 300 K (below 110 K the crystals break up owing to internal stress).

4. Conclusion

The temperature dependence of inhomogeneous broadening in equation (2) is governed by the $T_0 - T$ term and $g(T)$. In order to estimate the predicted behaviour in paradichlorobenzene, we find the value of the sums in (2).

S_{ki} and γ_k were unknown and equation (2) must be transformed to (Callen 1960,

Ashcroft and Mermin 1987)

$$A = c\nu_0(T_0 - T) \left| \sum_i \frac{1}{\nu_0} \frac{\partial \nu_0}{\partial \sigma_i} - \frac{g(T)}{C_V} \sum_i \alpha_i \right|.$$

The thermal dilatation tensor α_i , the specific heat C_V , ν_0 and $g(T)$ were obtained from the work by Wheller and Colson (1976), the *Journal of Physical and Chemical Reference Data* (1984) and Moross and Story (1966). If $\partial \nu_0 / \partial \sigma_i = 10 \text{ Hz cm}^2 \text{ kg}^{-1}$ (Zamar and Brunetti 1988) and with the values given above, the first sum in (2) is one order of magnitude greater than the second (over the whole temperature range); thus a linear behaviour is predicted just as observed experimentally.

The extrapolated inhomogeneous broadening in paradichlorobenzene in a ceramic matrix is, however, far from zero at $T = T_0$ and it cannot be predicted by our model. We suggest that this disagreement might be due to long-range strain fields at the ceramic-paradichlorobenzene interface which arise on the liquid-to-solid transition of paradichlorobenzene.

Acknowledgment

The authors wish to express their thanks to the Consejo Nacional de Investigaciones Cientificas y Tecnicas de Argentina for financial support.

References

- Ashcroft N W and Mermin N D 1987 *Solid State Physics* (Hong Kong: CBS Publishing ASI Ltd)
 Callen H B 1960 *Thermodynamics* (New York: Wiley)
 Das T P and Hahn E L 1958 *Solid State Phys. Suppl.* 1 (New York: Academic) 41-4
Journal of Physical and Chemical Reference Data 1984 vol 13, Suppl 1 (New York: American Chemical Society and American Institute of Physics)
 Kanert O and Mehring M 1971 *NMR Basic Principles and Progress* vol 3 (Berlin: Springer)
 Moross G G and Story H S 1966 *J. Chem. Phys.* **45** 3370
 Shulman R G, Wyluda B J and Anderson P W 1957 *Phys. Rev.* **107** 953
 Stoneham A M 1969 *Rev. Mod. Phys.* **41** 82
 Wang T C 1955 *Phys. Rev.* **99** 566
 Wheller G L and Colson S D 1976 *J. Chem. Phys.* **65** 1227
 Zamar R and Brunetti A H 1988 unpublished