

# Nuclear acoustic resonance measurements of the temperature dependent dynamic electric field gradient $V_{44}$ in palladium

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**Abstract.** We report on the temperature dependence of the relative electron contribution  $r_{44}$  to the dynamic electric field gradient  $V_{44}$  in single-crystal palladium. For this, NAR2 lineshape data (NAR  $\equiv$  nuclear acoustic resonance) are presented in the temperature range between 11 and 210 K. By extrapolation, the value of  $r_{44}$  at very low temperatures is found to fit well the systematic dependence of  $r_{44}$  on  $N(E_F)$  among the d transition metals.

## 1. Introduction

In palladium metal the results of many experiments like magnetic resonance, static magnetisation and propagation of ultrasound studies reveal a strong correlation of Knight shift  $K$  [1, 2] both with magnetic susceptibility  $\chi$  and the elastic constant  $c_{44}$  [3, 4], the reason for which is presumably the high density of states of d electrons and their high exchange interaction. The temperature dependence of  $K$ ,  $\chi$  and  $c_{44}$  is similar and shows a characteristic extremum at around 100 K. The explanation of this behaviour given in the literature is that it is due to the d-band structure and the high value of the density of states  $N_d$  near the Fermi energy  $E_F$  [3, 5].

Another quantity mainly determined by  $N(E_F)$  is the dynamic electric field gradient  $V_{44}$  [6] which we have measured by the nuclear acoustic resonance (NAR) signal intensity. In our experiments with Pd,  $V_{44}$  is generated by an ultrasonic shear wave propagating along the [110] direction in the FCC lattice, distorting the unit cell trigonally.  $V_{44}$  is composed both of a lattice contribution  $(V_{44})_{\text{latt}}$  arising from the distortion of the electric charge contribution in the vicinity of the atom under consideration, and of the conduction electron contribution  $(V_{44})_{\text{ce}}$  which comes from the deformation of the d electron cloud of the atom itself.

Hitherto, it could be demonstrated only for BCC metals like Mo, Ta, Nb and V that the relative contribution

$$r_{44} = (V_{44})_{\text{ce}} / [(1 - \gamma_\infty)(V_{44})_{\text{latt}}]$$

is directly proportional to  $N(E_F)$  [6].

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In most d transition metals, the temperature dependence of  $r_{44}$  is determined by lattice vibrations leading to an  $r_{44}(T) \sim T^{3/2}$  law like that for Ta [7]. However, since Pd has the highest value of  $N(E_F)$  among the d transition elements, one would expect  $r_{44}(T)$  to be dominated by band structure effects.

In the following, our NAR investigation of Pd shows that the systematics for  $r_{44}$  mentioned above, i.e.  $r_{44} \sim N(E_F)$  is also valid for Pd. Likewise, the temperature dependence of  $r_{44}$  we have found exhibits a peak in  $r_{44}(T)$  at around 100 K—similar to that of  $K(T)$ ,  $\chi(T)$  and  $c_{44}(T)$ .

## 2. Experimental details

The palladium single crystal we have used for the determination of  $r_{44}$  was the same as for previous NAR Knight shift experiments [8]. This crystal was cut in such a way that the ultrasonic wave vector  $\mathbf{q}$  was parallel to the [110] diagonal, with its polarisation vector  $\mathbf{u}$  parallel to the [001] direction while the crystal was oscillating at one of its natural frequencies. To generate transverse acoustic waves, an 8 MHz quartz transducer (AC-cut) was bonded to one of the flat end-faces of the crystal with liquid polymer LP32 (Thiokol). The small changes in the ultrasonic amplitude due to NAR absorption were observed using a MOUS-type spectrometer and a field modulation technique. The output signal of the marginal oscillator was fed into a lock-in amplifier so that in the end the registered signal was proportional to the field derivative of the absorption.

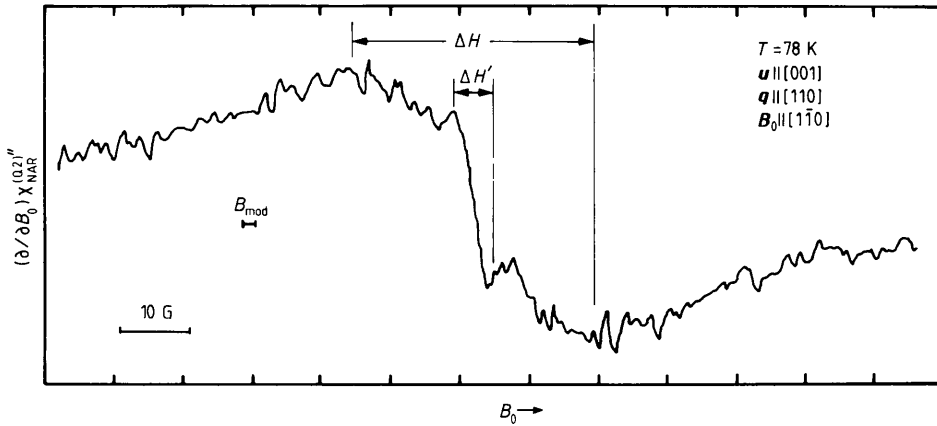
The coupling of the  $^{105}\text{Pd}$  nucleus via its quadrupole moment to the ultrasonically induced dynamic electric field gradient  $V_{44}$  strongly depends on the orientation of the crystal with respect to the magnetic field  $\mathbf{B}_0$ . Therefore, the alignment of the sample was chosen such that  $\mathbf{B}_0 \parallel [1\bar{1}0]$ , so as to maximise the probability of occurrence of transitions with  $|\Delta m| = 2$  (NAR2).

The signal was stored in a digital signal averager, and in order to increase the signal-to-noise ratio, was averaged and integrated to obtain the NAR signal intensity. Similarly, the non-resonant Alpher–Rubin acoustic absorption was registered as a calibration signal for the NAR intensity. This calibration technique is well known and is described elsewhere [9]. Its disadvantage, however, is that due to the high RRR value, the Alpher–Rubin attenuation becomes unobservably small at temperatures below 60 K. Therefore it was not possible to calibrate the NAR signals we have observed at 25 K and at 11 K.

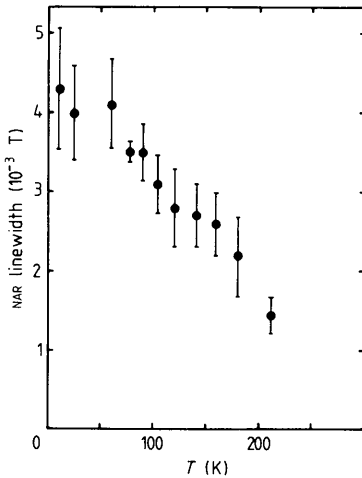
For future measurements this disadvantage could be overcome by generating a calibration signal in the MOUS spectrometer itself by electronic means, e.g. an impedance change of defined magnitude produced by a pin-diode network, a technique already suggested in the literature [10].

## 3. NAR Lineshape

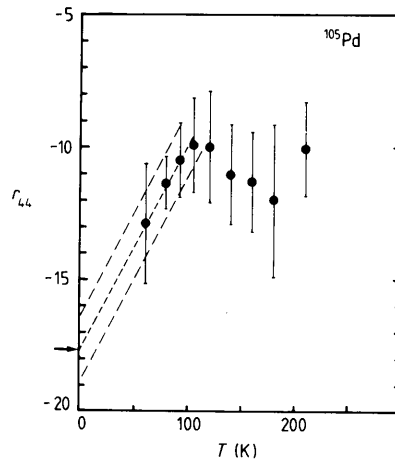
When NAR was first observed in palladium [8], the lineshape exhibited an unusual asymmetry that was probably distorted in part by considerable overmodulation. To solve the question of the true lineshape, an NAR2 line was registered using a very small modulation field ( $H_{\text{mod}} = 1.7$  G).



**Figure 1.** Observed field derivative of NAR2 absorption of palladium; transverse sound along the [110] axis, ultrasonic frequency  $\omega/2\pi = 8.3943$  MHz,  $(B_0)_{res} = 22.431$  kG, modulation field amplitude  $B_{mod} = 1.7$  G, modulation frequency  $\nu_{mod} = 37.5$  Hz, lock-in time constant  $\tau = 300$  ms, field sweep  $\Delta B_0/\Delta t = 10$  G/80 s. This spectrum was stored in 250 channels and averaged by taking 319 sweeps.



**Figure 2.** Temperature dependence of the NAR2 linewidth  $\Delta H$ .



**Figure 3.** Temperature dependence of  $r_{44} = (V_{44})_{ce}/[(1 - \gamma_{\infty})(V_{44})_{lat}]$ . The arrow denotes the extrapolated value of  $r_{44}$  at 0 K.

Figure 1 shows the original trace demonstrating that the NAR2 line at  $T = 78$  K is a superposition of at least two lines having equal resonance fields; a narrow one with  $\Delta H' = 5$  G and a wide one with  $\Delta H = 35$  G. The slight asymmetry of the narrow line might still be due to overmodulation effects.

Figure 2 shows the variation of  $\Delta H$  with temperature. Fluctuating electric field gradients produced by mobile hydrogen impurities are probably the reason for this temperature behaviour. The temperature dependence of the narrow line is not shown

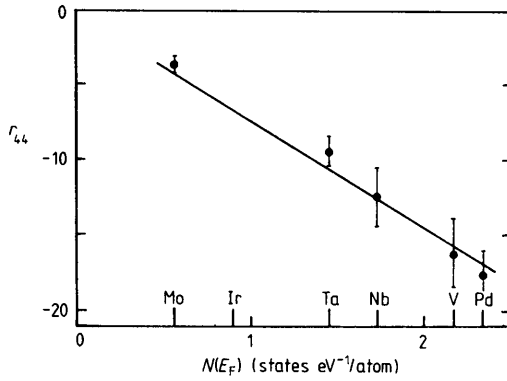


Figure 4. Systematic correlation of  $r_{44}$  with  $N(E_F)$  for the d transition metals.

here, since all the other spectra were taken with higher modulation field amplitudes ( $H_{mod} = 4\text{--}8$  G), so the narrow line could not be discerned.

#### 4. Dynamic electric field gradient $V_{44}$

The measurements presented in this paper were performed to verify whether the temperature dependence of  $r_{44}$  behaves similarly to  $K(T)$ ,  $\chi(T)$  and  $c_{44}(T)$ . To evaluate  $r_{44}$  from our measurements, the experimental data were processed and combined with other literature values as follows: first, the observed NAR signal trace has to be integrated twice after subtracting a suitable baseline which *a priori* is not known [9]. Secondly, when calibrating the NAR signal by Alpher–Rubin attenuation, the DC conductivity  $\sigma_{DC}$  is needed. The data for  $\sigma_{DC}$  have been taken from the literature [11]. Furthermore,  $(V_{44})_{latt}$  must be calculated and subtracted from the experimental value  $V_{44}$  in order to obtain  $(V_{44})_{ce}$ . For this, the ionic charge number was extracted from Hall effect data [12].

A decision has to be taken about the sign of  $V_{44}$ , as only  $(V_{44})^2$  can be determined from the experimental data.  $V_{44}$  was assumed to be positive, resulting in a negative  $r_{44}$  in accordance with the general systematics [13].

In figure 3 the temperature variation of  $r_{44}$  is presented, and, despite a relative error of between 9% at 78 K and 24% at 180 K,  $r_{44}(T)$  shows an extremum at 100 K and then decreases monotonically as the temperature is lowered.

We tentatively extrapolated  $r_{44}$  to very low temperatures in order to arrive at a value of  $r_{44}$  for  $T = 0$  K which refers to the density of states at the Fermi energy,  $N(E_F)$  [14]. The limit of  $r_{44}(T = 0$  K) was put into the systematics of  $r_{44}$  already found for other d transition metals [6, 15]. Figure 4 clearly shows that  $r_{44}(T = 0$  K) =  $-17.5 \pm 1.5$  fits very well into the systematics.

Our procedure leads to a discrepancy in numerical values of  $(V_{44})_{latt}$  calculated by the point charge model using Hall effect data at  $T = 0$  K, and on the other hand, using the extrapolated value of  $r_{44}(T = 0$  K). This could indicate that either care has to be taken for the calculation of  $(V_{44})_{latt}$  when using the Hall coefficient which varies rapidly below 60 K, or that the linear extrapolation is not correct at very low temperatures. This discrepancy could be clarified by providing more experimental NAR2 data below 60 K using the external signal calibration technique mentioned above.

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