MEASUREMENT OF SURFACE ACOUSTIC WAVES IN RARE EARTH METALS AT LOW TEMPERATURE

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ABSTRACT — The velocity and attenuation of a 5 MHz surface acoustic wave have been measured in polycrystalline Al, Gd and Tb as a function of temperature from 300-200 K. Similar measurements have also been made in the hexagonal basal plane of a single crystal of Tb. In all cases the results have been compared to calculations based on the bulk elastic moduli. In Al the agreement is good while in the two rare earth elements there are a number of discrepancies some of which can be understood in terms of the magnetic properties of these materials.

1 — INTRODUCTION

The surface properties of rare earth metals are particularly interesting for a variety of reasons. The elements are highly reactive and the surfaces can form oxides, hydrides, nitrides and carbides. While the oxides and nitrides are in higher concentrations close to the surface the hydrides are thought to be uniformly distributed throughout the materials.

Thermal cycling of the metals can produce residual stress which may be enhanced close to the surface [1]. In the magnetic phases, and particularly the spiral spin antiferromagnetic phase, it has been postulated that the magnetic structure of rare earth metals is different at the surface to that in the bulk of the material [2]. Finally the surface domain structure contains closure domains that are again different to the domain structure in the bulk of the material. Some of these surface properties can be studied by surface acoustic wave propagation, measuring the temperature dependence of the velocity V_s and attenuation α_s of the surface acoustic wave (SAW or Rayleigh wave).

There are a range of experimental techniques for launching and receiving SAWs but many of them are not suited to low temperature environments or to the study of small samples. After carefully investigating several techniques [3] we found that the angled transducer method could be used down to at least 200 K on samples with a dimension in the propagation direction of as little as 2-3 mm. To test the reliability of the technique, measurements were first of all carried out on a polycrystalline aluminium sample and the results compared to surface wave velocities calculated from bulk single crystal elastic constants.

Since our temperature range was limited to temperatures above 200 K then in order to study the effect of magnetic order on the surface wave propagation we restricted our attention to the two heavy rare earth metals Gd and Tb. Both crystalise in the hexagonal close packed structure with five bulk single crystal elastic constants C_{ij} [4]. Gd orders ferromagnetically at a Curie temperature T_c of 293 K with magnetic moments aligned along the hexagonal c-axis. Below a spin re-orientation temperature (T_{sr}) of 240 K the moments move away from c-axis to lie along an easy cone oriented at an angle Θ to the c-axis. Θ initially rises rapidly to an angle of $\sim 70^\circ$ before falling to $\sim 35^\circ$ where it remains down to 4.2 K.

Tb is paramagnetic down to Néel temperature (T_N) of $\sim$ 226 K where it orders in a spiral spin antiferromagnetic phase. This phase only exists over a small temperature range of approximately 7 K and below $\sim$ 217 K, the Curie temperature, Tb is a basal plane ferromagnet. The available temperature range therefore allowed study of magnetic phase changes of both Gd and Tb. We report here measurements of the temperature dependence of V_s and α_s in polycrystalline samples of Gd and Tb which are compared to surface wave velocities calculated from bulk single crystal and polycrystalline elastic constants. In addition we have measured the temperature dependence of the surface wave velocity in the basal plane of a single crystal sample of Tb which can be compared directly with calculated values.

2 — CALCULATION OF SURFACE WAVE VELOCITIES

In an isotropic medium a simple expression relates the surface acoustic wave velocity to the bulk longitudinal and shear velocities (V_L and V_T respectively):

$$(2 - V_S/V_T)^2 = 4\ [1 - (V_S/V_L)^2]^{1/2}\ [1 - (V_S/V_T)^2]^{1/2} \qquad (1)$$

The longitudinal bulk wave velocity is related to the bulk modulus K and the shear modulus G by:

$$V_L = [(K + 4/3\ G)/\rho]^{1/2}$$

where ρ is the sample density. The shear wave velocity is given by

$$V_T = [G/\rho]^{1/2}$$

Hill [7] pointed out that the bulk and shear moduli can be calculated from the single crystal elastic constants by taking the mean of the two approaches adopted by Voigt [8] and by Reuss [9]

$$K = 1/2\ (K_V + K_R) \quad ; \quad G = 1/2\ (G_V + G_R)$$

In the case of a hexagonal crystal, for example, one has for the Voigt approach:

$$K_V = 1/9\ \ [C_{33} + 2\ (C_{11} + C_{12} + 2\,C_{13})]$$

$$G_V = 1/15\ [C_{33} + 2\ (C_{11} - C_{12} - 2\,C_{13})] + 1/5\ [2\,C_{44} + C_{66}]$$

while, following Reuss,

$$1/K_R = 2\,S_{11} + S_{33} + 2\ (S_{12} + 2\,S_{13})$$

$$1/G_R = 4\ [S_{33} - S_{12} + 2\ (S_{11} - S_{13})] + 3\ [2\,S_{44} + S_{66}]$$

where the C_{ij} are the five independent elastic stiffness moduli $[C_{66} = 1/2\ (C_{11} - C_{12})]$ of the hexagonal symmetry and S_{ij} are the elastic compliance moduli defined by

$$S_{ij} = (-1)^{i+j}\ \Delta C_{ij}/\Delta C$$

where ΔC is the determinant of the C_{ij} and ΔC_{ij} is the minor of the element C_{ij}. Hence it is a straightforward matter to calculate the surface acoustic wave velocity in an isotropic polycrystal form the single crystal moduli.

The study of surface wave propagation in hexagonal single crystals involves numerically complex computation to obtain the surface wave velocities. It is normal to use a «surface Green's

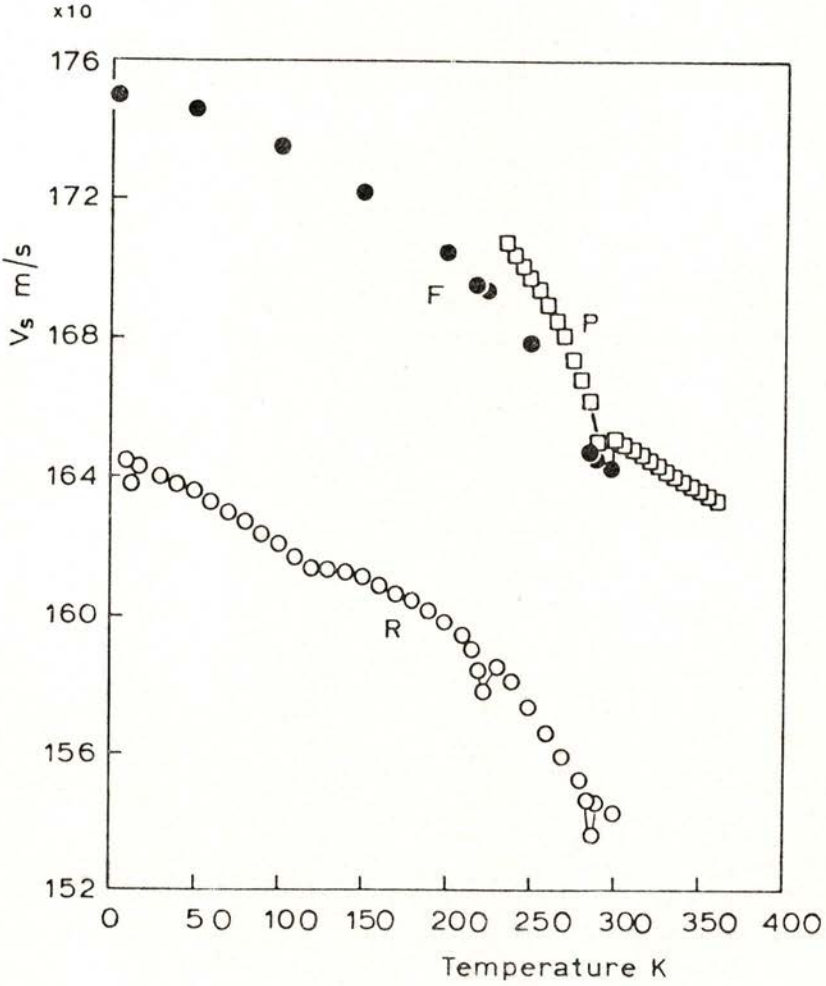

Fig. 1 — Computed Isotropic Surface Wave Velocity in Gadolinium Versus Temperature: □ Data from S. B. Palmer, [4]; ○ Data from M. Rosen, [11]; ● Data from E. S. Fisher, [10].

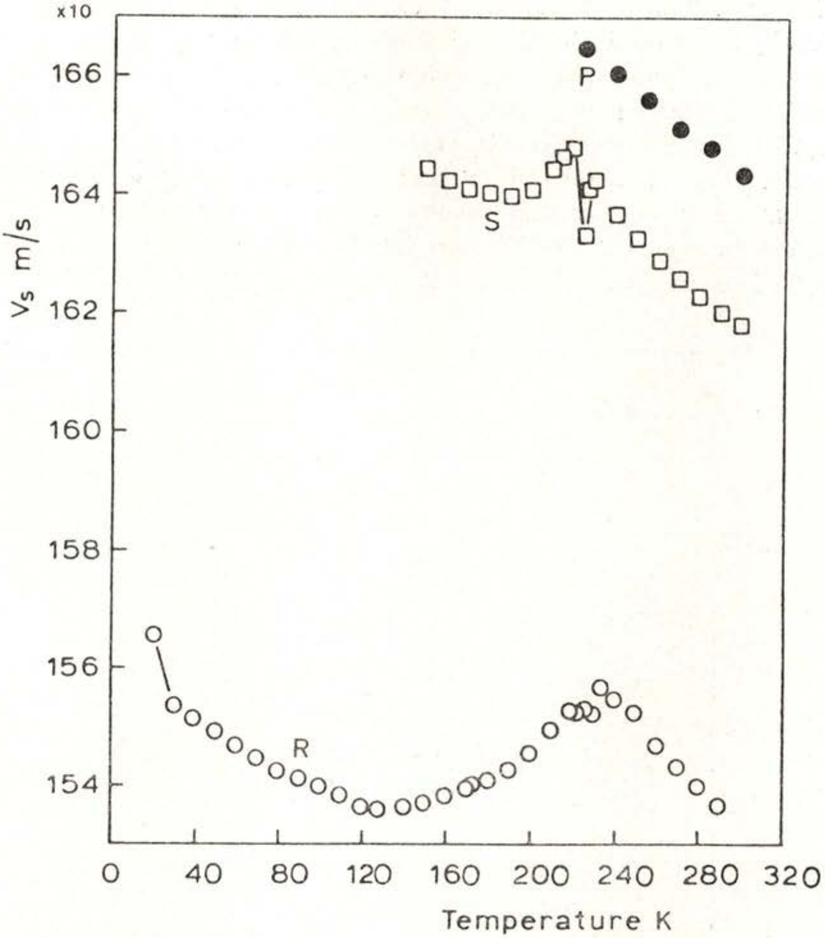

Fig. 2 — Computed Surface Wave Velocity in Polycrystal Terbium for Different Temperatures: □ Data from K. Salama, [12]; ○ Data from M. Rosen, [11]; ● Data from S. B. Palmer, [4].

function approach» where the velocity formula can be transformed to an algebraic equation similar to that of the isotropic case [10]. The most simple solution is obtained for propagation of surface waves in the basal plane of the hexagonal crystal which is transversely isotropic. The relationship between V_S and the C_{ij} can be written

$$C_{33}\,(V_S^2 - C_{44}/\rho)\,(V_S^2 - C_{11}/\rho + C_{13}^2/C_{33}\rho) = C_{44}\,V_S^4\,(V_S^2 - C_{11}/\rho) \quad (2)$$

This is a bicubic equation in V_S and it is interesting to note that by using the isotropic limit one can derive eq. (1) from eq. (2).

Fig. 1 shows the computed isotropic surface wave velocity in Gd obtained from eq. (1) using two different sets of single crystal elastic constants [4], [11] and the polycrystalline data of Rosen [12]. It can be seen that the polycrystalline values lie below the single crystal results which are themselves in fair agreement. Gaps in the data are due to one or more of the single crystal constants being unavailable due to experimental problems.

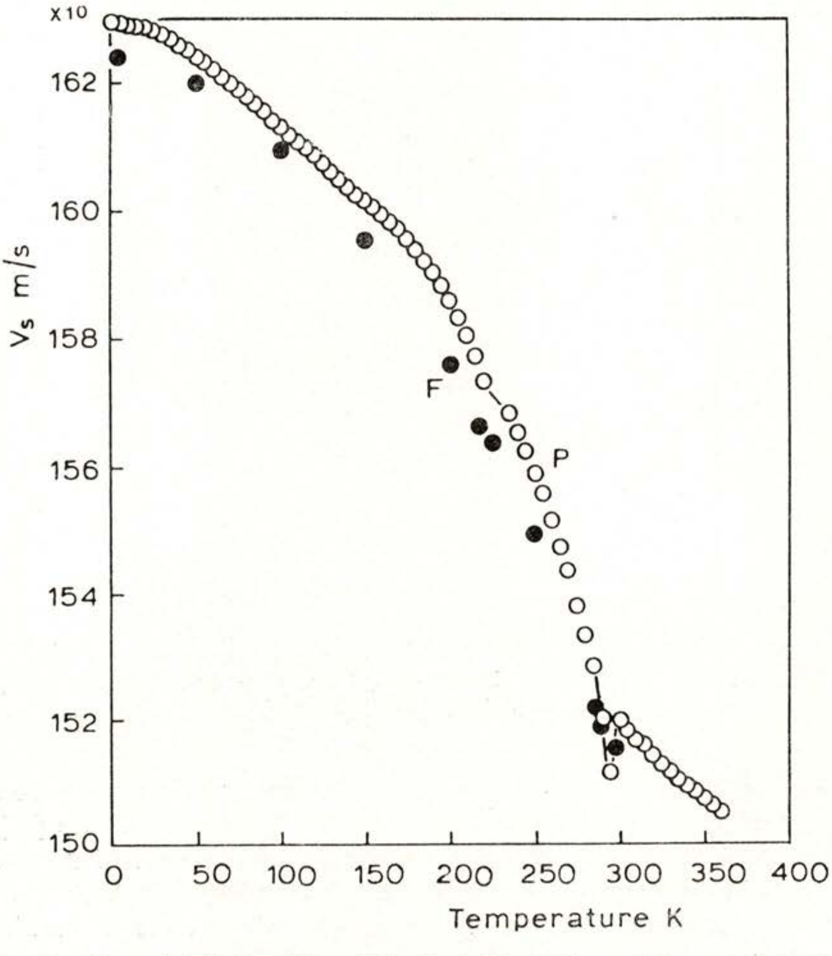

Fig. 3 — Computed Surface Wave Velocity in Basal Plane of Hexagonal Single Crystal of Gadolinium as a function of temperature:
○ Data from S. B. Palmer, [4]; ● Data from E. S. Fisher, [10].

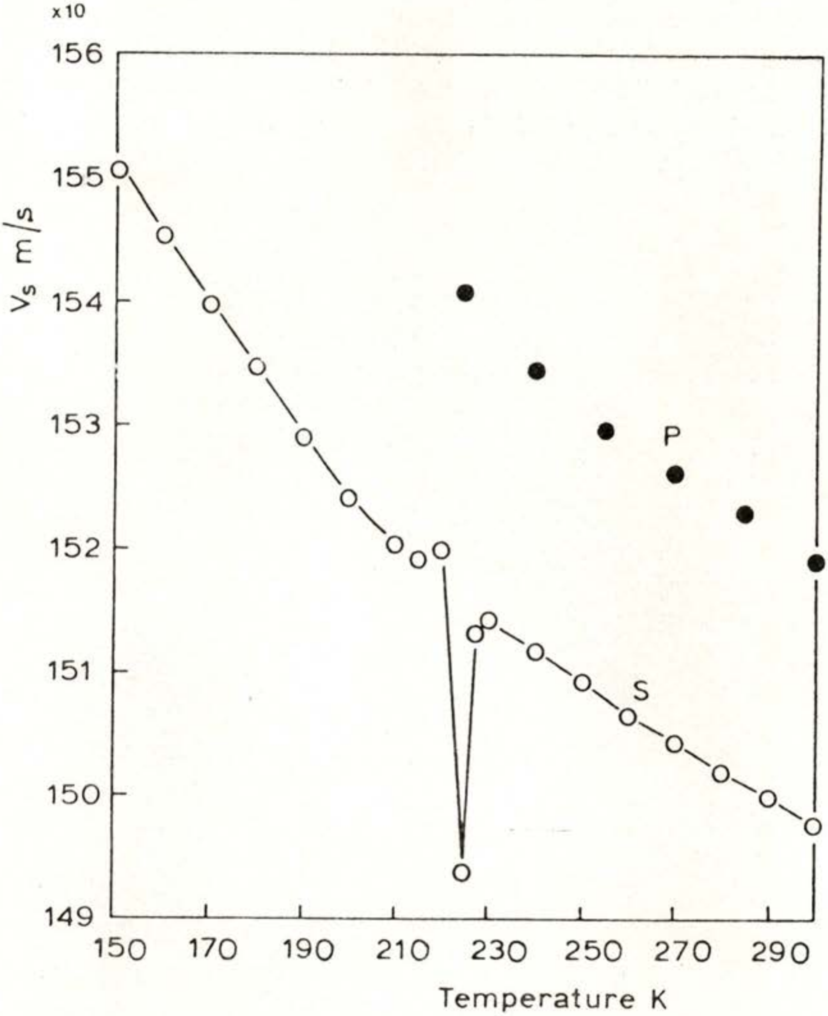

Fig. 4 — Computed Surface Wave Velocity in Basal Plane of Terbium Single Crystal as a function of temperature:
○ Data from K. Salama, [12]; ● Data from S. B. Palmer, [4].

Fig. 2 shows similar data for Tb where again Rosen's polycrystalline results [12] lie well below the values calculated from the single crystal elastic constants [4], [13]. In Fig. 3 we plot the computed surface wave velocity in the basal plane of the single crystal Gd computed from the available single crystal data [4], [11]. Fig. 4 shows a similar calculation for Tb. Anomalies are observed in all four figures which can be attributed to the magnetic phase changes described earlier. In all the figures the individual points have been calculated from the tabulated data in the papers, leading to widely spaced points in some cases. Rosen does not give tabulated points and these have been estimated from the published figures.

3 — EXPERIMENTAL DETAILS

The surface acoustic waves were launched and detected using plate transducers mounted at an angle of 45° on opposite edges of the sample (Fig. 5). The transducers operated in a compressional mode at a resonant frequency of 5 MHz and were fabricated from PZT 5A ceramic. The transducer was bonded to the edge of the sample with Rapid Araldite which provided a long bond life over an appreciable temperature range. Masking tape was used whilst the araldite was setting to prevent spreading onto the sample surface. The two opposing edges of the sample were lapped

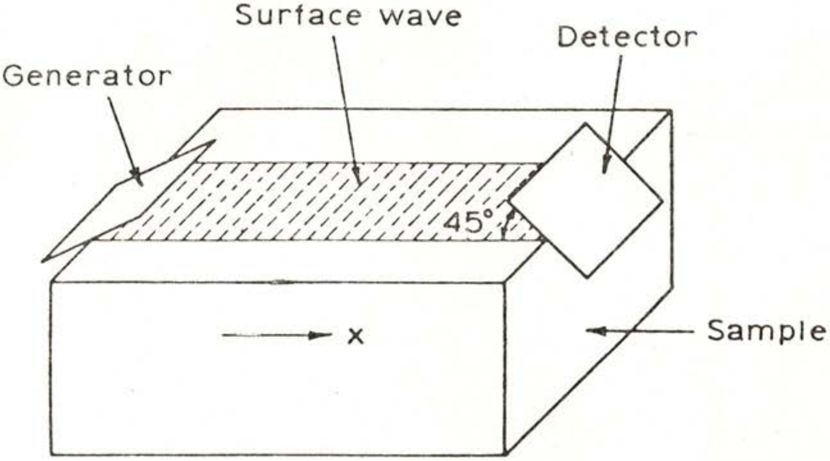

Fig. 5 — Schematic diagram of angled transducer arrangement for surface wave experiment.

parallel to optical tolerances; in all cases parallelism of better than 15 seconds of arc was achieved. The sample surface that supported the surface wave was polished to a flatness of better than one tenth of the acoustic wavelenghth ($\lambda/10 \sim 30\ \mu$). Normally flatness of better than $5\ \mu$ was achieved. The polycrystalline samples of Al, Gd and Tb were prepared using standard diamond cutting and diamond lapping techniques, after which they were etched and annealed. For the rare earths a standard etch of a 50-50 solution of acetic and nitric acids was used and annealing took place at approximately 60°C for 5 hours [1]. The single crystal of Tb was spark planed to its final shape at the Centre for Materials Science, University of Birmingham. It was tetragonal with surfaces perpendicular to the a, b and c axes.

To generate the surface acoustic wave the transmit transducer was excited by a 5 MHz R.F. pulse of 0.5 μs pulse width and 25 volt peak height, from an Exact pulse generator (Model 7260). The pulse repetition frequency was ~ 20 Hz allowing the surface wave echoes to decay before the next pulse packet was launched. The transit time of the pulse was measured with the time delay facility of an oscilloscope. Due to problems of attenuation and pulse interference the transit time could only be measured from the initial launching of the surface wave to the first surface acoustic wave arrival at the detector.

Temperatures were maintained with a standard cold finger cryostat [14] in conjunction with a commercial temperature controller. Temperature measurement was achieved with two copper contantan thermocouples, one measuring the sample temperature, the other the environmental temperature. Temperature measurements were accurate to ± 1 K with point to point sensitivity of better than 0.2 K.

The major contribution to the errors in the measurement of the absolute velocity of the SAW arises from the location of the corresponding points on the initial generating pulse and the transmitted SAW signal.

One could be out by ± 1 cycle leading to an absolute error in V_s of $\pm 7\,\%$ in a typical sample. If the appropriate cycles are correctly identified the absolute error reduces to $\pm 0.4\,\%$ and arises from bond errors associated with the coupling of the trans-

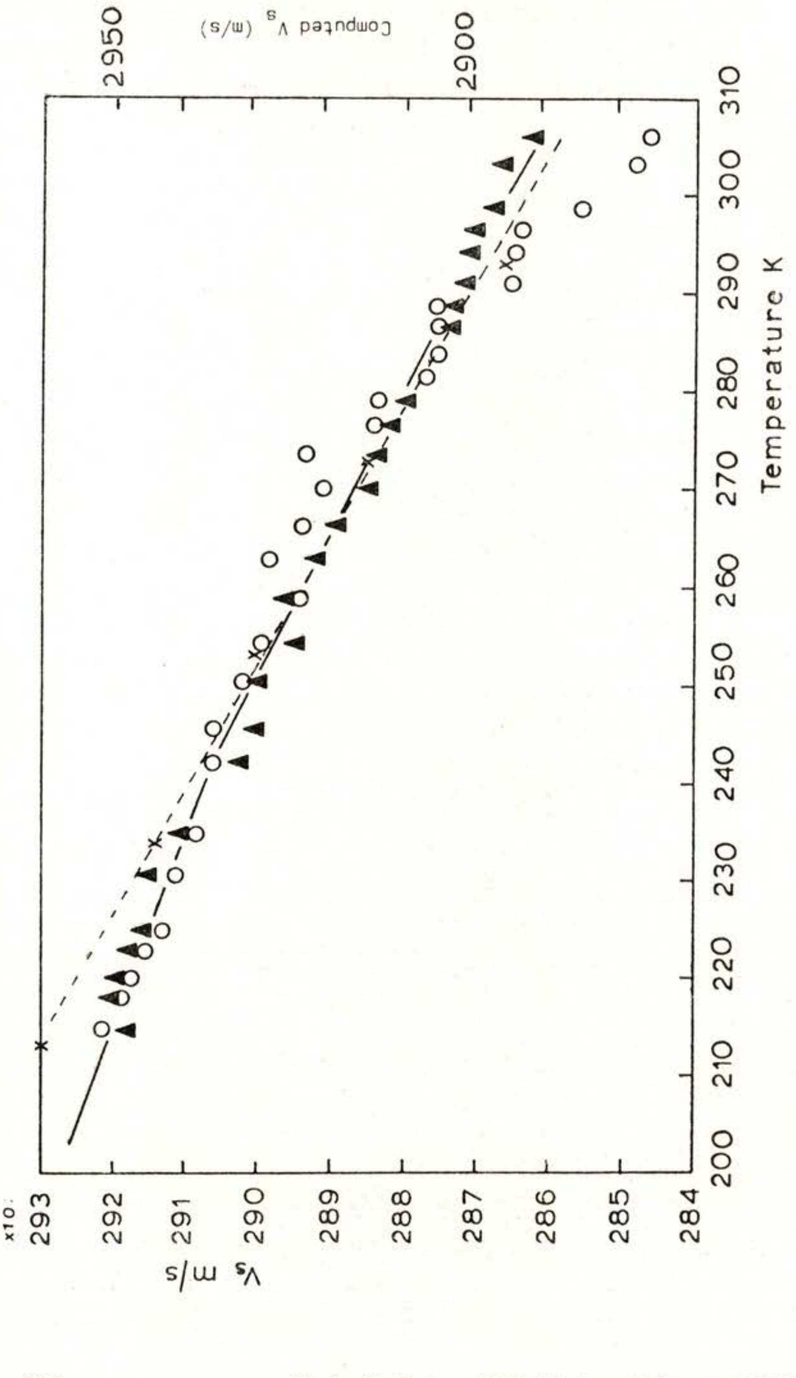

Fig. 6 — Comparison between three measurements of SAW velocity in Al. as a function of temperature. Solid line: Rel. V_s solid bond and ▲ Rel. V_s liquid bond, ○ ABs. V_s solid bond. X - - - Computed V_s from single crystal data of Sutton [14].

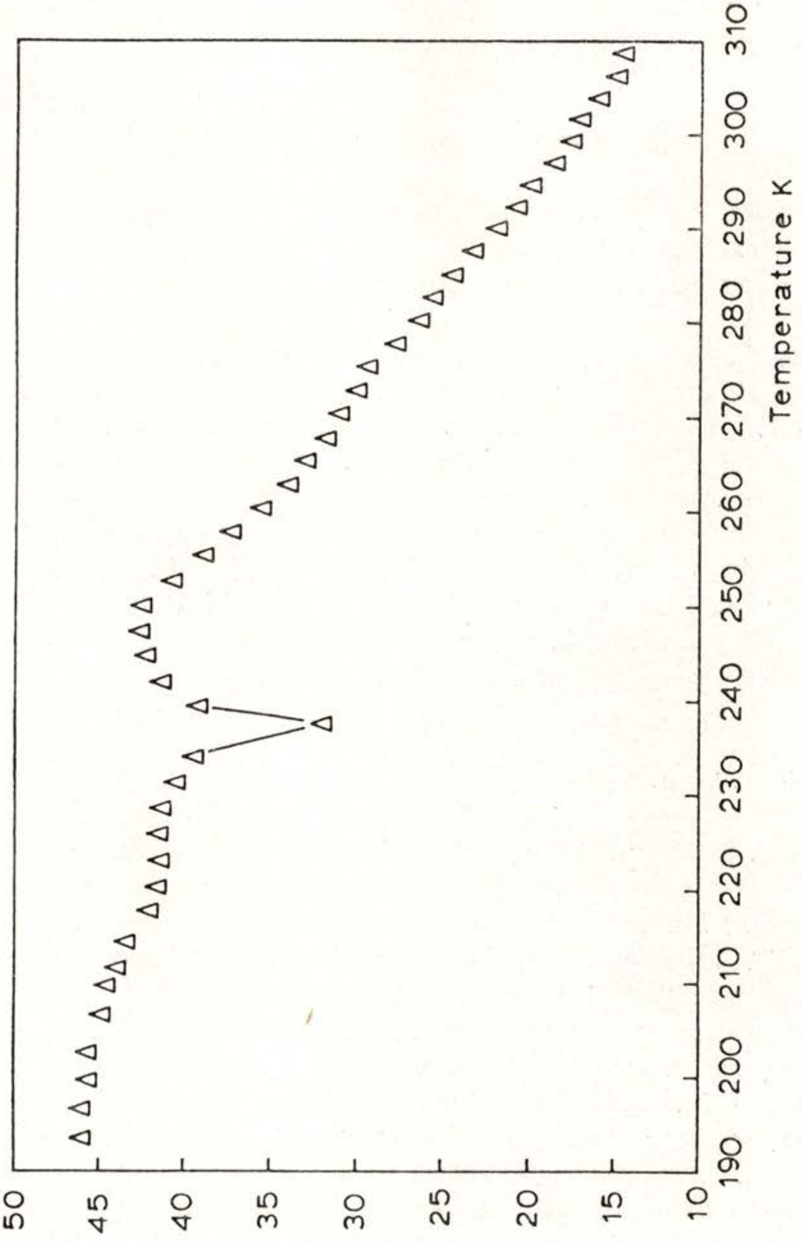

Fig. 7 — SAW Amplitudes in Al for different temperatures. Angled transducers. Lubricant oil bond.

ducer to the sample and from timing errors. This value is reduced still further when one is only interested in the point to point accuracy.

4 — RESULTS AND DISCUSSION

Initial experiments were carried out using a polycrystalline aluminium sample with a range of bonding agents between the transducer and sample edge. The temperature dependence of V_s with both an oil bond and an araldite bond are shown in Fig. 6 where they are compared to values calculated, via eq. (1), from the single crystal elastic constants. The absolute values differ by ~ 1 %, while the temperature dependence of the experimentally determined and calculated values of V_s are in good agreement. However when one measures the signal amplitude as a function of temperature, which should be related to the surface wave attenuation α_s, it is immediately obvious (Fig. 7) that the oil bond is not suitable since the mininum in α_s at ~ 240 K is produced by the solidification of the oil bond. All reliable measurements were therefore carried out with a Rapid Araldite bond.

Gadolinium

Fig. 8 shows the temperature dependence of V_s and α_s for the surface acoustic wave in the sample of polycrystalline Gd. The insets indicate that there are only minor anomalies at both T_c and T_{sr}. The measured V_s is in good agreement at room temperature with the value calculated from single crystal elastic constants, and appreciably higher than the polycrystalline calculations (Fig. 9). In contrast to Al the temperature dependence of the measured V_s is at least a factor three greater than the calculated values, which are themselves consistant. This difference is far in excess of what one might expect from experimental errors.

The measured relative attenuation obtained from the amplitude of a single pulse is compared in Fig. 10 to the polycrystalline results of Rosen [12]. In all cases the ordered phase produces an increase in the ultrasonic attenuation.

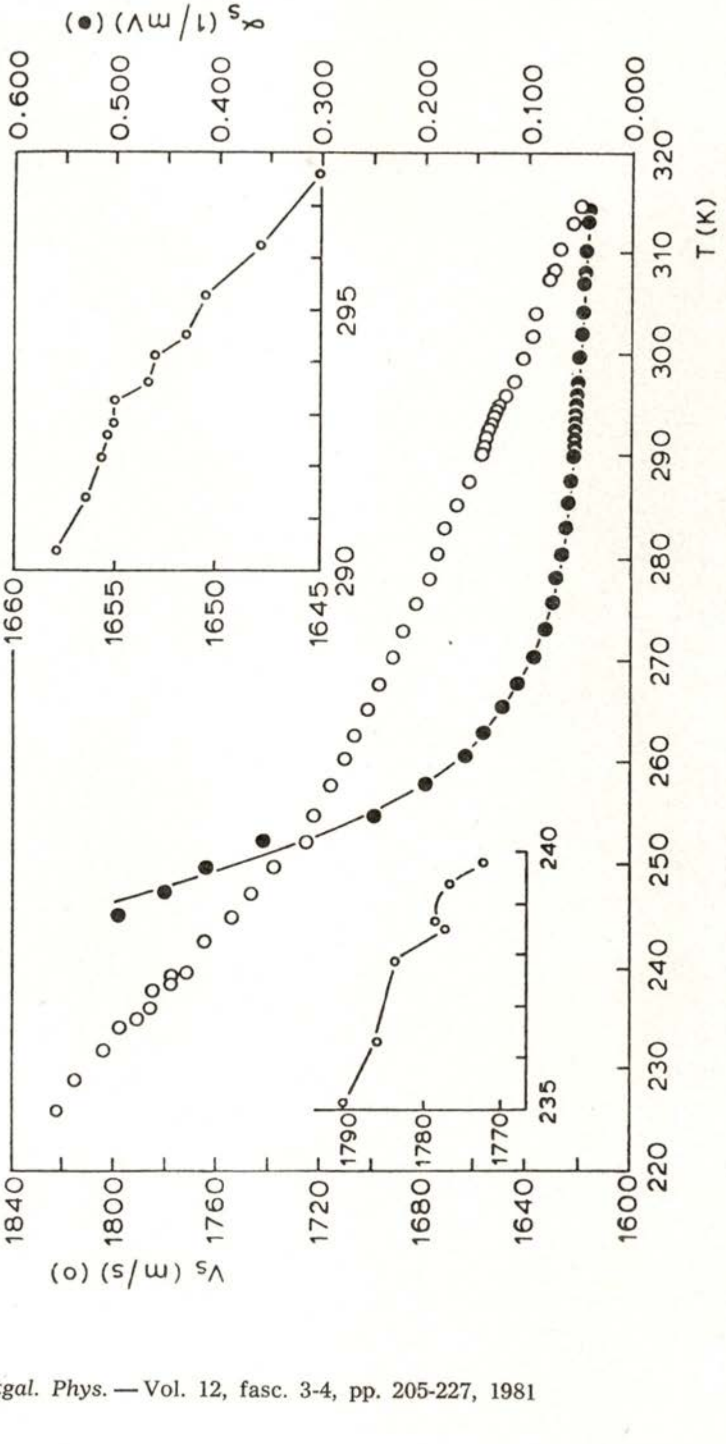

Fig. 8 — Surface acoustic wave propagation in polycrystalline gadolinium. ○ velocity; ● relative attenuation.

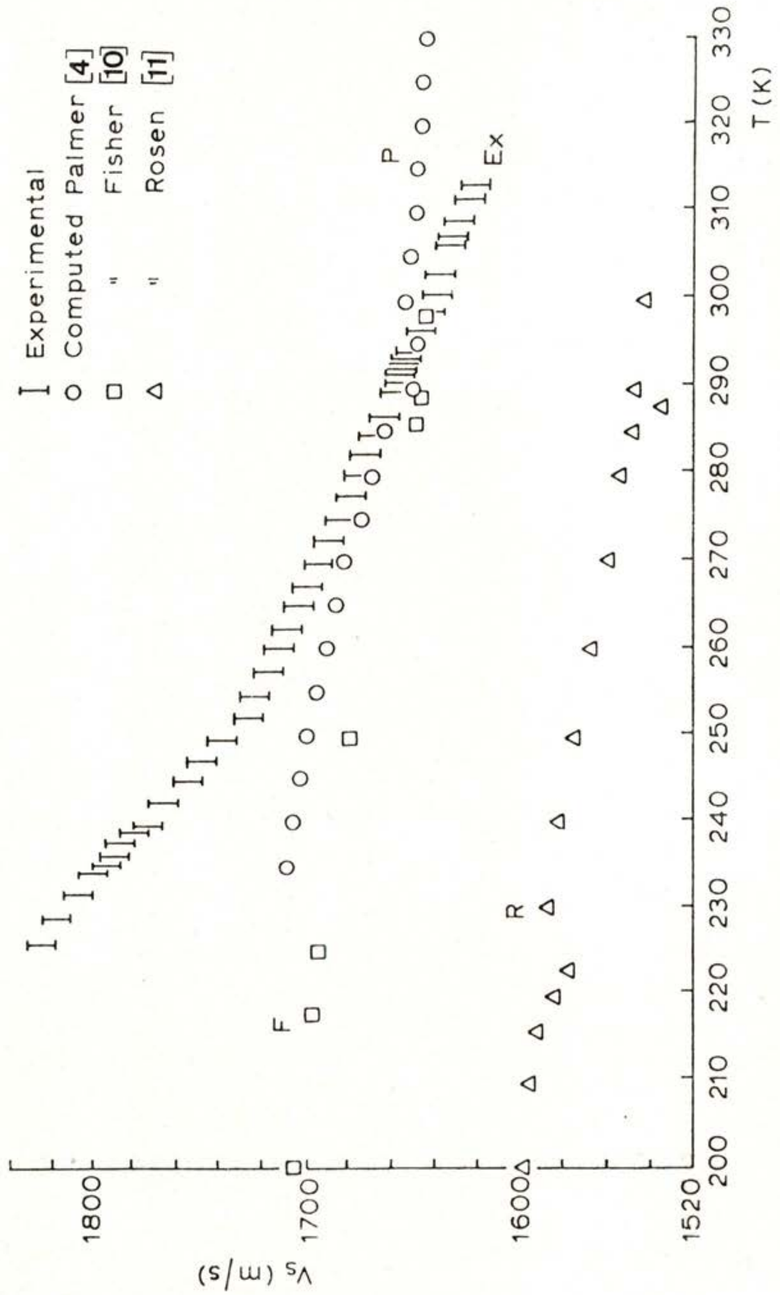

Fig. 9 — Polycrystalline gadolinium. Comparison of Experimental and Computed Values of V_s.

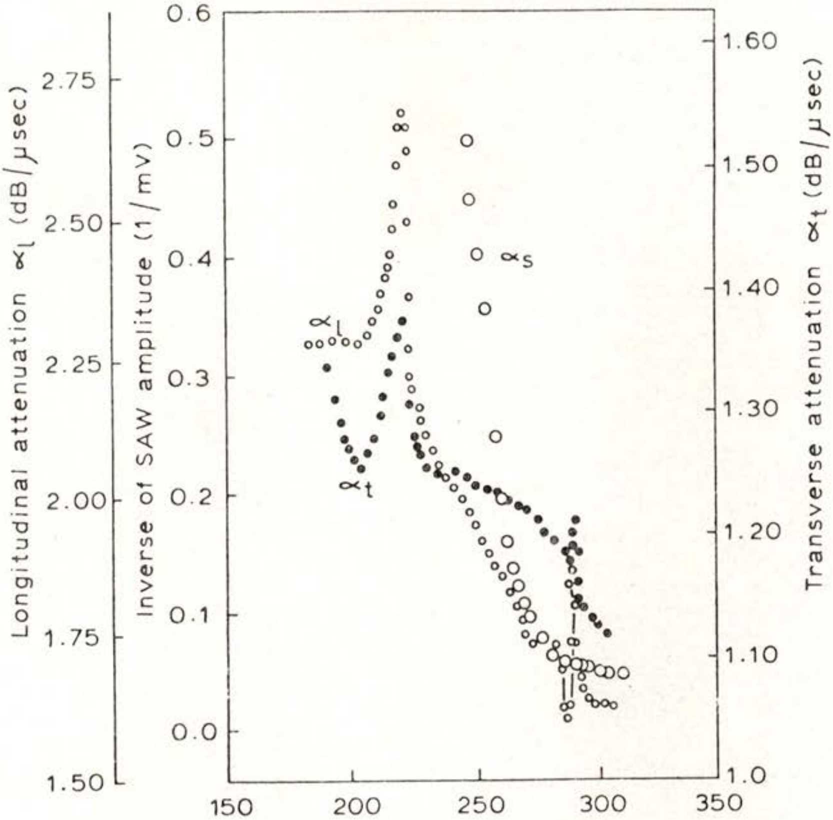

Fig. 10 — Comparison of inverse SAW amplitude (α_s) and bulk wave attenuation (α_l , α_t) from Rosen [11].

Terbium

The temperature dependence of V_s and α_s for polycrystalline Tb is show in Fig. 11. In the paramagnetic phase V_s increases with decreasing temperature in a similar manner to Gd. In contrast, however, there is a rapid decrease in V_s in the antiferromagnetic phase which is accompanied by an increase in α_s. Both changes are somewhat modified by the onset of ferromagnetism at ~216 K. When compared to calculated values (Fig. 12) V_s increases much more rapidly in the paramagnetic phase and in addition decreases much more rapidly in the ordered phases. The minimum observed at T_N for the calculated surface wave velocity

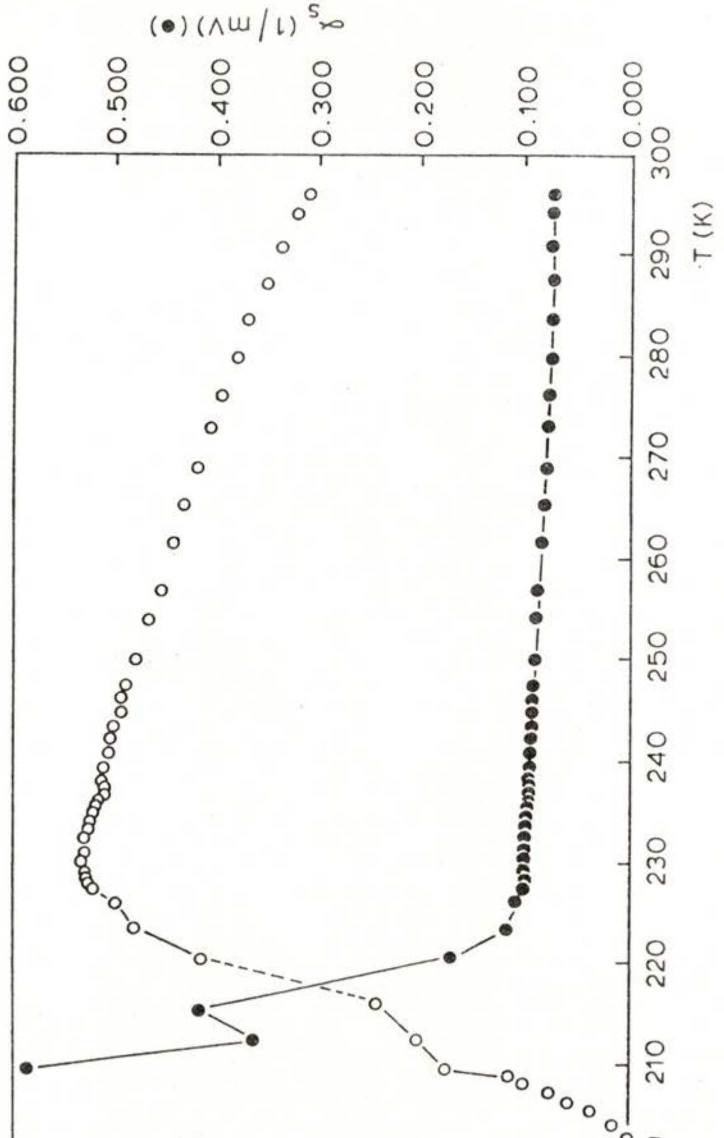

Fig. 11 — Surface acoustic wave propagation in polycrystalline terbium: ○ velocity; ● relative attenuation.

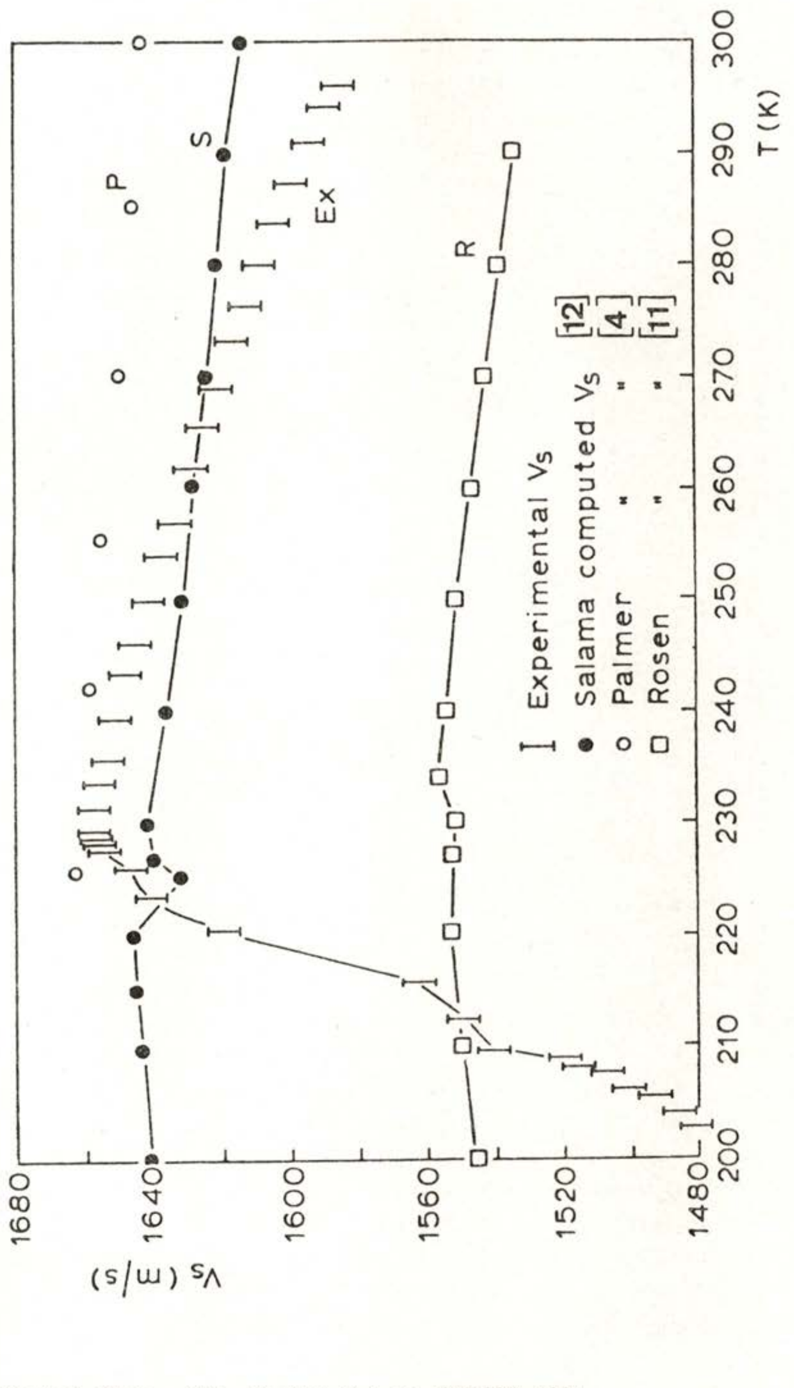

Fig. 12 — Polycrystalline terbium, comparison of experimental and computed values of V_s.

is much weaker than the measured decrease. It is difficult to make any suitable comment on the absolute values of the different curves with such a wide variation between the different sets of data although again the measured values are in better agreement with the calculations based on the single crystal elastic constants.

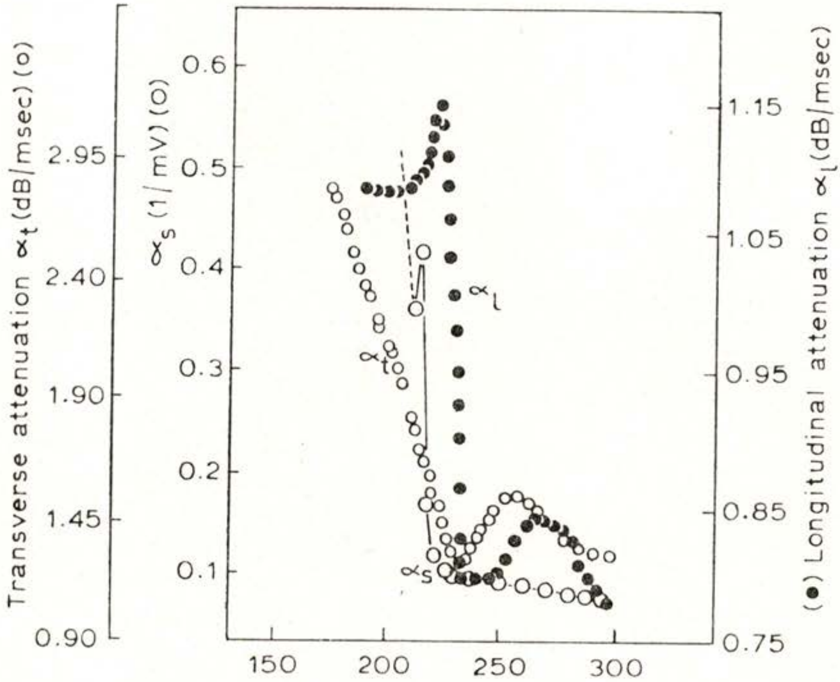

Fig. 13 — Comparison of inverse SAW amplitude (α_s) and bulk wave attenuation (α_l , α_t) from Rosen [11].

The temperature dependence of α_s (Fig. 13) shows some of the characteristics of both the longitudinal and shear wave propagation, as is to be expected for an acoustic mode that contains elements of both atomic displacements. The surface wave attenuation shows no evidence of any peaks in attenuation above T_N as is observed with the bulk waves.

The single crystal of Tb available for the propagation of a surface acoustic wave in the basal plane had a dimension of only 2.2 mm parallel to the propagation direction. This is approaching the limit of the present experimental technique and the results

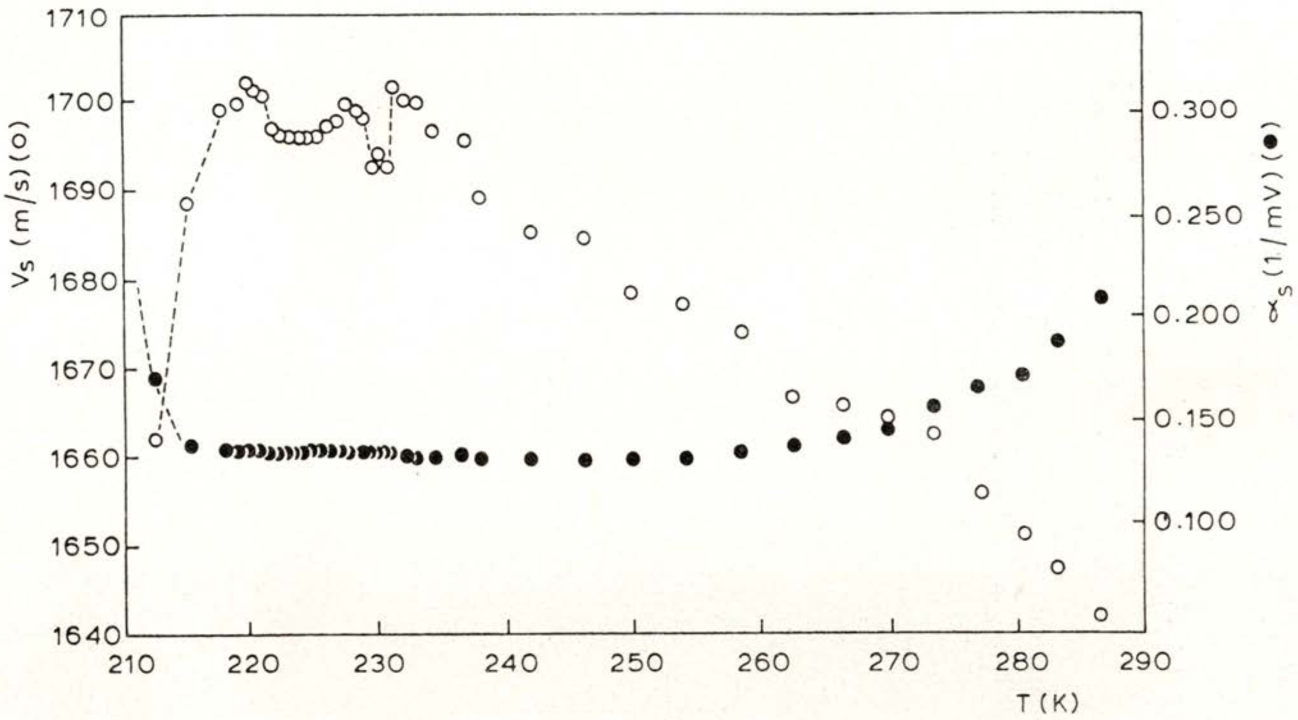

Fig. 14 — Surface acoustic wave propagation in the basal plane (parallel to ‘b’ direction) in single crystal terbium
○ velocity ● relative attenuation.

are therefore less reliable than the polycrystalline measurements. The temperature dependence of both V_s and α_s, propagating parallel to a 'b' direction are shown in Fig. 14. The onset of magnetic order produces marked changes in V_s in the region of T_N and a rapid decrease at T_c. In contrast the attenuation of the wave is only affected well below T_c. A comparison of V_s with calculated values from single crystal elastic constants, using eq. (2), indicates again that the temperature dependence of V_s is much higher in the paramagnetic phase than one would expect from bulk calculations (Fig. 15). The large discrepancy between the absolute values

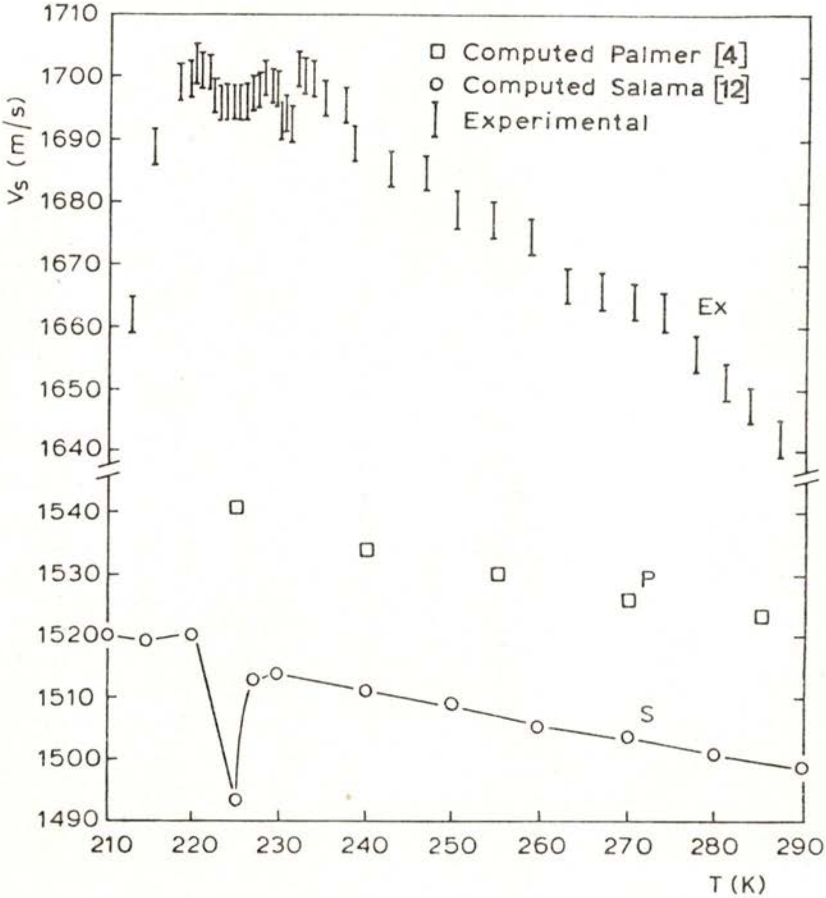

Fig. 15 — Single crystal terbium: comparison of experimental and computed values of V_s for propagation in the basal plane.

of V_s is probably due to the small sample length available which will enhance the errors introduced by bond effects and timing problems.

We have demonstrated for the first time that the magnetic phase changes in the rare earth metals are reflected in the properties of surface acoustic wave propagation, although the nature of the changes observed are not always what one would predict from bulk wave behaviour. Nevertheless in the ordered regions these differences may well be due to magnetic domain properties and to magnetic stresses localised in the surface. Evidence for the presence of these surface stresses can be found in measurements of the surface wave velocity at room temperature before and after a low temperature run.

TABLE 1 — SAW velocity at room temperature before and after low temperature run (L.T.R.): Tb single crystal, propagation along b-axis, in the basal plane

Day	Procedure	S.A.W. Velocity m/s	Temperature K
Day 1	Measured velocity followed by L.T.R.	1642	286.6
Day 2	Measured velocity followed by L.T.R.	1637	284.8
Day 3	Measured velocity followed by L.T.R.	1625	285.7
Day 4	Measured velocity	1619	287.2
Day 7	Measured velocity	1642	286.8

Table I shows the effect on V_s of repeated thermal cycling down to 200 K on the Tb single crystal. It is observed that V_s decreases after a low temperature run and that repeated thermal cycling over a period of four days produced a total decrease in $V_s \sim 1.3\,\%$. At the end of the fourth day the sample was allowed to remain in the cryostat at room temperature and after a further three days the SAW velocity was again measured at room temperature and was found to have recovered its original value. Some of this annealing of the residual stresses may have taken place in the araldite bond but it is more likely that the majority is produced by stress relief of the sample. No such effects have been observed in bulk ultrasonic propagation indicating that we are dealing with a surface phenomenon.

The behaviour of both Gd and Tb in the paramagnetic phase is rather more puzzling. For the cubic Al the calculated and measured values of V_s have the same temperature dependence in the paramagnetic phase. This is not the case for the hexagonal Gd and Tb where in every instance the measured temperature dependence is in excess of the calculated value. For different elements and for different crystallographic directions in a single element the ratio of experimental to computed gradients varied from 1.5 to 4 indicating again that it could not be an experimental error. There are two possible origins for these differences, either the mechanical properties of the surfaces of these rare earth metals are markedly different to the bulk or the theoretical expressions available for the calculation of V_s are in error. Further work in in progress to illuminate these possibilities.

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