

Figure 1. High pressure  $^{27}\text{Al}$  NMR in K Al alum, at 2.1 k bars. Centrefield: 6300 G; scan range: 200 G; time constant: 30 sec; Scantime: 60 mts,  $\nu = 7.000$  MHz

recorder were used. An external PAR lock-in amplifier was used for signal amplification, with reference (modulation) frequency optimised to  $\sim 80$  Hz. Its output was fed to the Varian recorder.

Figure 1 shows the  $^{27}\text{Al}$  signal obtained in K Al alum. Time constants of 30 sec were used, with sweep times of one hour, and a field sweep over 200 Oersteds.

The values of  $e^2qQ/h$  at several pressures were obtained by the above manner (table 1). The value of the coefficient of variation of  $e^2qQ/h$  with pressure was 0.021 kHz/bar. The explicit contributions to the variation of  $e^2qQ/h$  with  $T$ , i.e. purely due to vibrational effects accompanying variation of temperature can be obtained from the equation of state

$$\left[ \frac{\partial}{\partial T} \left( \frac{e^2qQ}{h} \right) \right]_{\nu} = \left[ \frac{\partial}{\partial T} \left( \frac{e^2qQ}{h} \right) \right]_P - \frac{3\alpha}{\beta} \left[ \frac{\partial}{\partial P} \left( \frac{e^2qQ}{h} \right) \right]_T$$

where the first term on the right side is the temperature variation at constant pressure (obtained from Weiss' study<sup>1</sup>) and the second term is the implicit contribution due to change in lattice dimensions (and obtained from our study).  $3\alpha$  is the volume thermal expansion and  $\beta$ , the bulk compressibility. The implicit and explicit contributions were found to be  $-0.11$  kHz/K and  $+1.03$  kHz/K respectively, to yield the temperature variation of  $e^2qQ/h$  at a constant pressure as 0.92 kHz/K.

Analysis in terms of the explicit and implicit contributions explains a somewhat unexpected observation in alums. Generally, in an ionic solid, one would expect (and confirmed in most other systems) that as temperature is raised, the ions would move out and the e.f.g. at

the nuclear site would decrease. However, in alums the e.f.g. is found to increase with temperature. This is explained for the first time by our experiment. The implicit contributions do have a negative sign, as expected, since these contributions arise from the actual thermal expansion of the lattice. However, the overwhelming contribution is from the explicit vibrational effects, and this has a positive sign, leading to an overall increase of e.f.g. with increase of pressure.

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## DEFORMATION-INDUCED STRUCTURAL TRANSFORMATION IN 99.2% PURE YTTERBIUM

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It is well known that at room temperature and atmospheric pressure ytterbium has an fcc structure<sup>1,2</sup>. The hcp structure associated with low and high temperatures has often been considered to be impurity stabilised<sup>3,4</sup>. However, Bucher *et al* report<sup>5</sup> the occurrence of this hcp phase in very high purity ytterbium also. They observe that a small amount of this hcp phase coexists with the major fcc phase at room temperature. In this paper, we report the effect of mechanical deformation on the fcc and the hcp structures coexisting at room temperature, viz 25°C.

Table 1. Variation of  $e^2qQ/h$  of  $^{27}\text{Al}$  in K Al alum

Pressure (kb).	0	1.155	2.162	4.175	5.182	6.189
$e^2qQ/h$ (kHz):	401	424	447	489	505	514

Results from x-ray diffraction, differential scanning calorimetry and optical micrographs have been used.

The majority of samples used in our experiments were 99.2% pure. The major impurities were Ca (0.42%) and Eu (0.19%). The minor impurities constituted by Fe, K, Al, Cr, Ti, Ce, Sm, Y, La, Mn, Zn, Mg, Pb and W were 0.2% in aggregate (Private communication). Cylindrical specimens were pressed between flat surfaces and the amount of deformation produced corresponded to a 75–80% reduction in the sample's thickness. X-ray diffraction patterns were recorded on a Philips powder diffractometer, Debye Scherrer Camera and Laue back reflection camera. Both  $\text{CuK}\alpha$  and  $\text{CrK}\alpha$  radiations were used. The DSC curves were traced from 300° to 900°K on a Perkin Elmer DSC II instrument at a heating rate of 20°K/min.

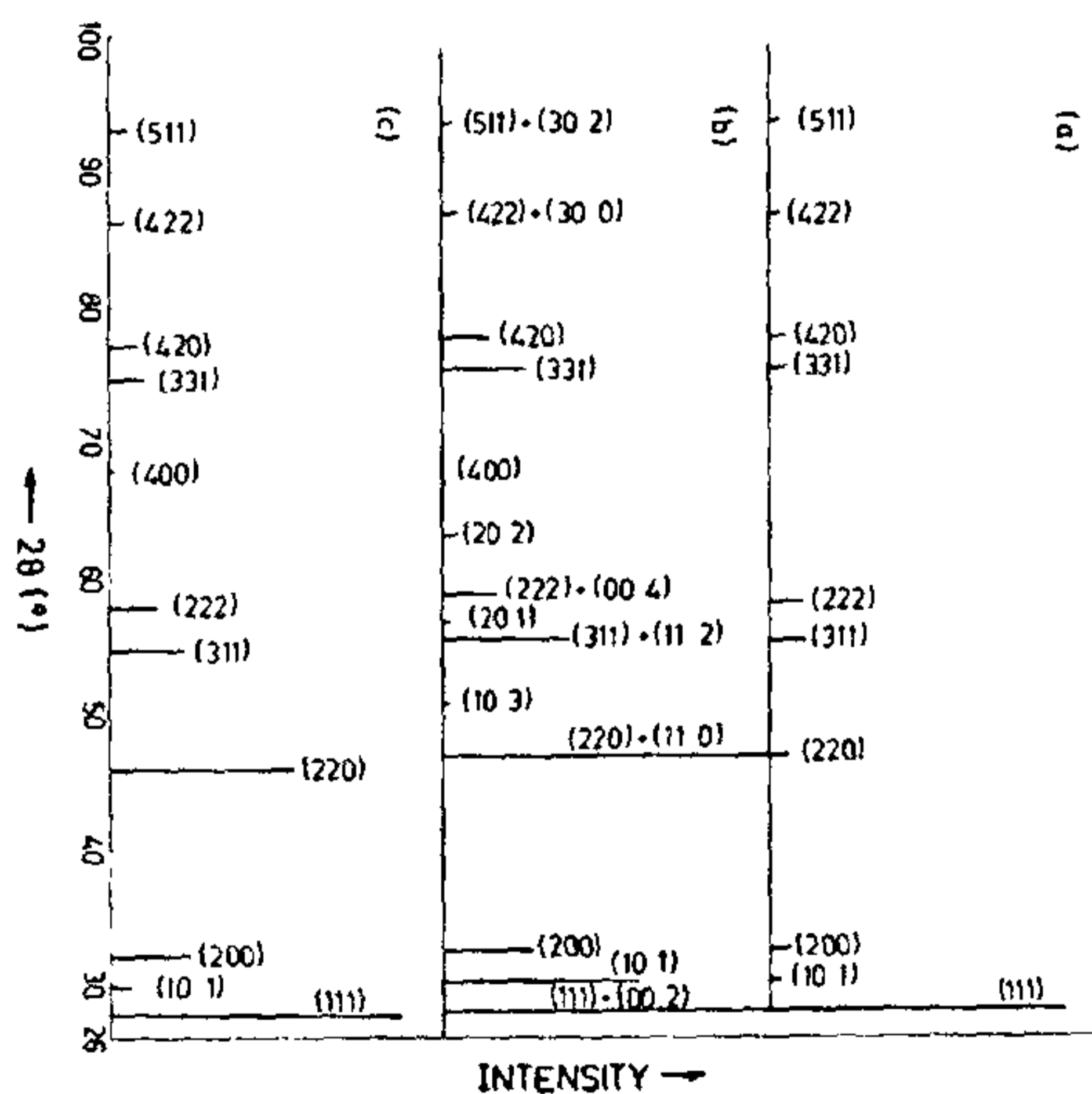
There is considerable overlap in the reflections from the fcc and the hcp phases, in the  $2\theta$  range examined by us. Some of the non-overlapping reflections are  $(002)_{\text{fcc}}$ ,  $(004)_{\text{fcc}}$ ,  $(10.0)_{\text{hcp}}$ ,  $(10.1)_{\text{hcp}}$ ,  $(20.1)_{\text{hcp}}$ ,  $(20.2)_{\text{hcp}}$ ,  $(20.3)_{\text{hcp}}$ . X-ray diffraction patterns recorded from samples prior to and after the deformation are presented in figures 1a and 1b respectively. The diffraction pattern in figure 1a is characteristic of the fcc structure. The presence of a small amount of the hcp component

is indicated by the occurrence, albeit faintly, of the most intense reflection,  $(10.1)$  from the hcp phase. The striking difference between figures 1a and 1b is due to the change in the distribution of intensities. In particular, the enhancement in the intensity of the non-overlapping hcp reflections suggests that the deformation induces a transformation of the type  $\text{fcc} \rightarrow \text{hcp}$ . The intensity distribution in figure 1b also suggests the presence of texture in the sample. Occurrence of both the deformation-induced transformation and texture has been confirmed by photographic methods also.

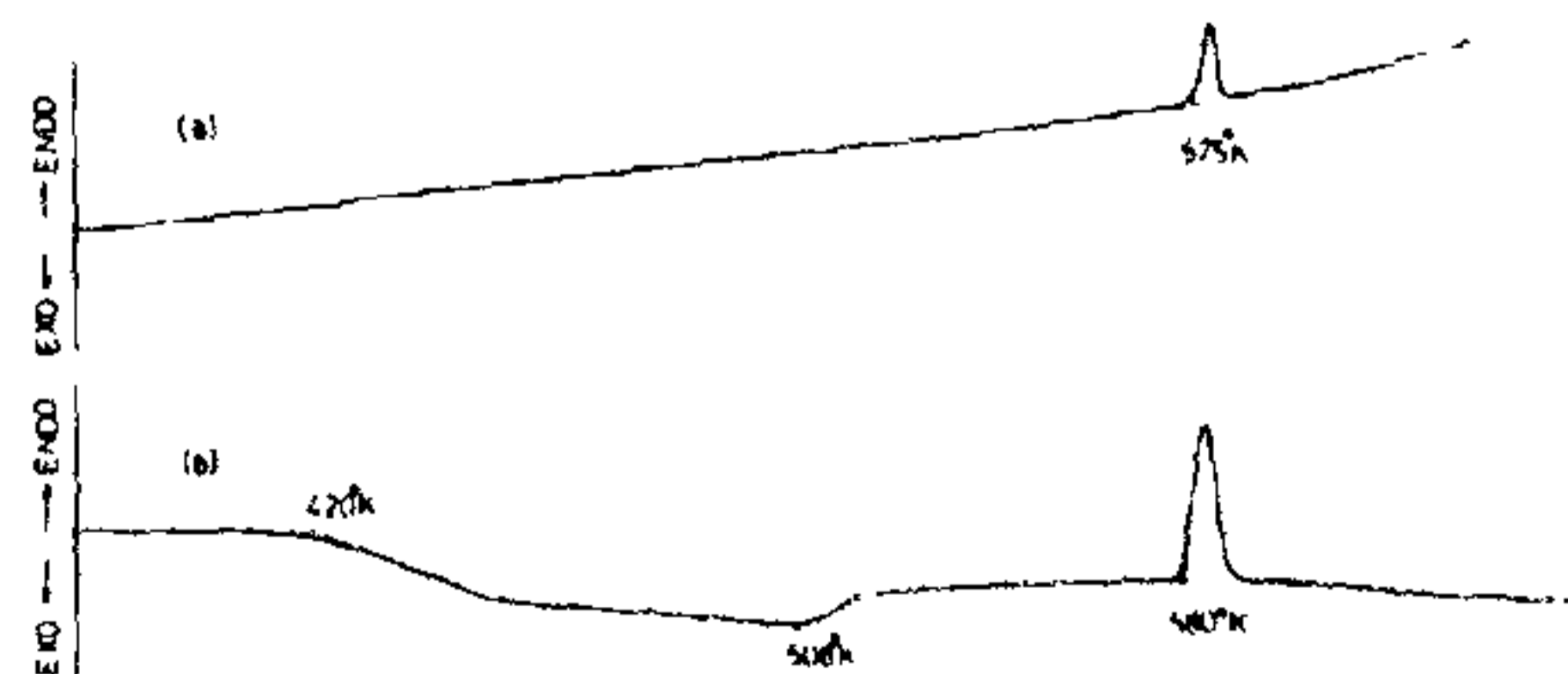
It must be mentioned that the  $\text{fcc} \rightarrow \text{hcp}$  transformation was often only partial. However, the overall enhancement of the intensities of the reflections from the hcp phase was a feature consistently observed with both thin (thickness  $t < 1 \text{ mm}$ ) as well as thick ( $t \geq 4 \text{ mm}$ ) specimens.

The deformation-induced transformation is confirmed by the differences in the characteristics of the DSC curves recorded from the undeformed and the deformed samples (figures 2a and 2b). The common peak at 580°K corresponds to the well known  $\text{fcc} \rightarrow \text{hcp}$  transformation at high temperatures<sup>3</sup>. In the DSC curve from the deformed sample, there are two additional broad peaks at  $\sim 400^\circ\text{K}$  and  $\sim 510^\circ\text{K}$  respectively. The peak at 400°K refers to the recrystallization observed in deformed ytterbium samples (unpublished). The DSC peak at  $\sim 510^\circ\text{K}$  has been found to correspond to a reverse transformation of the type (hcp) deformation induced  $\rightarrow \text{fcc}$ . The x-ray diffraction pattern recorded at 523°K (figure 1c) characterises this fcc phase.

Further evidence for the deformation-induced transformation is obtained from the microstructures. Figure 3 is the photomicrograph from the undeformed sample. The microstructure is characteristic of twinning within the grains. Similar twinning in thin films of ytterbium has been reported by Gasgnier and



**Figure 1:** X-ray diffraction patterns from (a) undeformed ytterbium sample (b) the deformed ytterbium sample and (c) the deformed ytterbium sample heated to 523°K. The lines from the oxide have been omitted in (c).



**Figure 2:** DSC curves from (a) the undeformed and (b) the deformed ytterbium samples.



Malaurent<sup>6</sup>. The microstructure of the deformed specimen shown in figure 4 does not indicate the presence of twinning and is distinctly different from that in figure 3. The photomicrograph in figure 5 is from the deformed sample heated just beyond the (hcp) deformation induced  $\rightarrow$  fcc transformation temperature and it indicates the presence of a major fcc phase and some oxide.



Figures 3–5: Photomicrographs from the (3) undeformed, (4) deformed and (5) the deformed ytterbium samples heated beyond the hcp  $\rightarrow$  fcc transformation.

It has been observed that the deformation-induced fcc  $\rightarrow$  hcp transformation occurs only in samples with high impurity content. X-ray patterns recorded from 99.92% pure ytterbium specimens obtained from Rare Earth Products Limited have shown that as in less pure specimens, the initial structure corresponds to a major fcc phase and a small amount of the hcp component. However, on deformation, there was no change in the intensities of the hcp reflections.

The deformation-induced transformation in the 99.2% pure specimens and the retention of the hcp component in the 99.92% pure specimens observed by us are not in conformity with the results of Bucher *et al*<sup>5</sup>, who reported the complete removal of the hcp component by plastic deformation, in 99.95% pure, condensed films of ytterbium. The significant differences between Bucher's and our experiments concern the sample thickness and the impurity contents. It appears, therefore, that the minor hcp component gets easily stabilized on plastic deformation in ytterbium samples with large amounts of impurities. The exact role of the impurity atoms in inducing the transformation is yet to be understood. Larger sample thickness also appears to facilitate the deformation-induced transformation.

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