PRESSURE DEPENDENCE OF ²⁷Al NMR IN POTASSIUM ALUMINIUM ALUMS

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THE interaction of quadrupole moments of nuclei with the electric field gradients at the sites of such nuclei provides a means of probing the latter in solids. Thus, in alums, the axial crystal fields at trivalent ion sites can be monitored through the NMR of ²⁷Al nuclei ($I = 5/2$). Weiden and Weiss[1,2] have made detailed measurements of ²⁷Al NMR in alums at various temperatures. However, the temperature dependence of the quadrupolar coupling constant which has contributions from volume effects and explicit dependence on vibrations cannot be analyzed into its component parts by a temperature variation study alone. A simultaneous study of the pressure dependence permits a complete analysis, and the results of such a study, done for the first time, are being reported in this communication.

The ²⁷Al nucleus in alums

The ²⁷Al nucleus has a nuclear spin $I = 5/2$, with 100% abundance. Its NMR frequency is 11.094 MHz for a 10 K Oersted field, and its sensitivity is 3.04 times that of the proton at constant frequency. The study of ²⁷Al NMR in alums is made specially difficult because of the fact that in the alum unit cell containing four formula units of K Al(SO₄)₂ . 12H₂O out of a total of $4 \times 48 = 192$ atoms only four are ²⁷Al. Further reduction is caused by the fact that there are four inequivalent sites for the ²⁷Al nucleus, each of which gives five lines, to a total of 20 lines in general.

The Al site in K Al alum has a predominant cubic component with a perturbing trigonal axial field. The latter, on interacting with the ²⁷Al nucleus, in a quadrupolar perturbed NMR experiment, gives rise to five equally spaced lines. The spacing of the lines yields the e.f.g. q according to the relation:

$$v_m = \frac{3(2m-1)}{2I(2I-1)} \times \frac{e^2 qQ}{h} \times \frac{3\cos^2\theta - 1}{2},$$

where $(3\cos^2\theta - 1)$ factor arises out of the angle θ between the principal axis of the e.f.g. and the magnetic field, (and the rest of the symbols have their usual meaning).

The large number of lines arising from a general orientation of the crystal with respect to the magnetic field can be reduced to a simple five line spectra, (with consequent enhancement of S/N ratio) by proper angular orientation. The axis of rotation chosen for this set of experiment was the [1 1 0] direction. In this configuration, the plane of rotation contains two of the body diagonals having an acute angle of 70° 32′ between them. When the magnetic field direction bisects this acute angle between the body diagonals, an interesting case of coincidence occurs. The projection of all the four body diagonals, two in the plane of rotation and two out of it, have a value cos 35° 16′ times the principal value of the e.f.g. This leads to a coincidence of transitions for each of four inequivalent sites in the unit cell, with a consequent increase of the S/N ratio. The (1 1 0) face is also easy to grind.

The high pressure NMR experiment

Large single crystals (∼ 1.5 cm edge) of K Al(SO₄)₂ . 12H₂O were grown by slow evaporation from a saturated solution of the constituents. A cylindrical shape, along the [1 1 0] axis had to be ground out to give the maximum filling factor for the NMR tank coil.

The high pressure cell used for the experiment was made out of Be-Cu, annealed to a Rockwell hardness of RC 39 ∼ 40. It has been described in detail elsewhere[3]. It had a locknut configuration, such that angular orientational studies could be easily carried out by rotating the magnet about the vertical axis of the pressure cell. The r.f. lead entered the cell through a quartz capillary high pressure seal in the bottom-plug. One end of the r.f. tank coil was soldered to this r.f. lead while the other to a ground stub fixed on the face of the bottom plug. One of the strong points in the design of this cell was the soldered joints of the tank coil, such that there was no deterioration of the Q of the coil when attached to the pressure cell. A further advantage was in the fact that the large space available in the cell did not damp the r.f. to any extent, such that the signal was just as strong inside the cell as outside. Paraffin oil was used as the pressure transmitting medium such that single crystal work could be carried out without the crystal cracking from non-hydrostaticity of pressure.

The tank coil was part of a home-made low level Robinson oscillator. This oscillator was mounted on top of the magnet pole-gap such that the magnet could be easily rotated. A Varian 9 inch magnet along with its power supply, Field Dial Hall probe regulator and
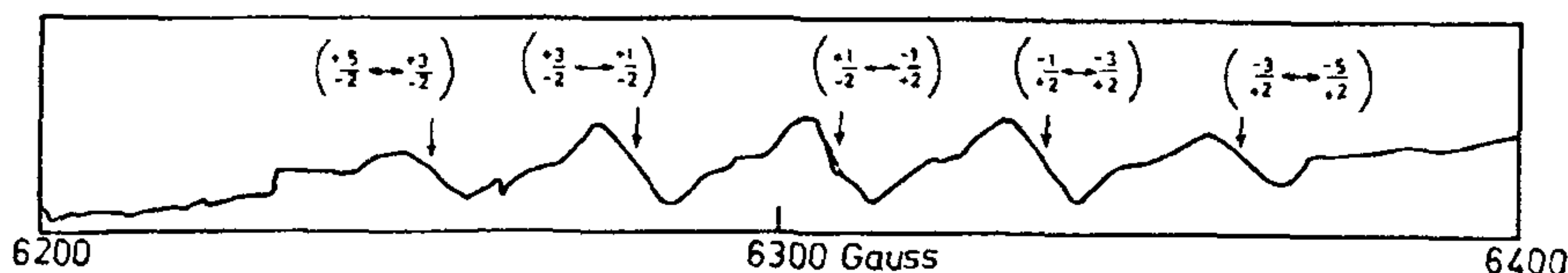
Figure 1. High pressure ^{27}Al NMR in K Al alum, at 2.1 k bars. Centrefield: 6300 G; scan range: 200 G; time constant: 30 sec; Scantime: 60 mts, $v = 7.000$ MHz

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

Figure 1 shows the ^{27}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

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

where the first term on the right side is the temperature variation at constant pressure (obtained from Weiss' study[1]) and the second term is the implicit contribution due to change in lattice dimensions (and obtained from our study). 3α is the volume thermal expansion and β, 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[1,2]. The hcp structure associated with low and high temperatures has often been considered to be impurity stabilised[3,4]. However, Bucher *et al* report[5] 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}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